2005 Architectural Coatings Survey

DRAFT Reactivity Analysis

January 2007

California Environmental Protection Agency

Air Resources Board

State of California
California Environmental Protection Agency
AIR RESOURCES BOARD

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ARB, Board	Air Resources Board
ASTM	American Society for Testing and Materials
CAS#	Chemical Abstract Service number
MIR	Maximum Incremental Reactivity
NOx	Nitrogen Oxides
O_3	Ozone
RRAC	Reactivity Research Advisory Committee
SCAQMD	South Coast Air Quality Management District
SCM	Suggested Control Measure
SWA	Sales-Weighted Average
SWAMIR	Sales-Weighted Average Maximum Incremental Reactivity
TPD	Tons Per Day
U.S. EPA	United States Environmental Protection Agency
VOC	Volatile Organic Compound

Executive Summary

In April 2005, the Air Resources Board (ARB or Board) conducted a survey of companies that sold architectural coating products in California in 2004 (ARB, 2006.) The survey gathered detailed ingredient information for the volatile compounds contained in each coating product. ARB staff used these ingredient data to analyze the photochemical reactivity (i.e., ozone-forming potential) associated with architectural coatings. This document is intended to provide different options for evaluating the reactivity of architectural coatings, but it is not a formal regulatory document.

When coatings are applied, they release different types of organic compounds that can react in the atmosphere to produce different amounts of ozone. This ozone forming potential is called hydrocarbon reactivity and it is determined by the photochemical reactions in the atmosphere. If a coating contains a small amount of a highly reactive compound, it could have a relatively high reactivity rating even if it has a low level of volatile organic compounds (VOCs). Similarly, a coating that has a high VOC content may have a relatively low reactivity rating, if it contains compounds that aren't very reactive.

The ARB has pioneered the use of reactivity in regulations controlling VOC emissions. In 1991, the Board approved the Low Emission Vehicles and Clean Fuels regulation that allowed for the use of reactivity adjustment factors (ARB, 1990.) In June 2000, the Board approved a reactivity-based regulation for aerosol coatings (ARB, 2000.) This regulation was approved by the United States Environmental Protection Agency (U.S. EPA) in 2005 (U.S. EPA, 2005.)

In 2005, the U.S. EPA published a guidance document regarding the use of innovative reactivity-based approaches to achieve ozone reduction (U.S. EPA, 2005a.) This guidance encourages states to consider photochemical reactivity when developing control measures for state implementation plans (SIPs). U.S. EPA provided the following ways that reactivity could be addressed during the SIP development process:

- Develop speciated emission inventories to help identify the most reactive VOCs.
- Prioritize control measures based on reactivity.
- Target emissions of highly reactive VOCs with specific control measures.
- Encourage VOC substitution using reactivity-weighted emission limits.

U.S. EPA's guidance document supports the approach in ARB's Aerosol Coatings Regulation, which establishes reactivity limits based on individual ingredients rather than total VOC mass-based limits.

Architectural coatings are a large source of VOC emissions. Except for consumer products, it is the largest single source of VOC emissions among all stationary and area sources. In 2004, architectural coatings and associated solvents emitted approximately **95** tons per day from coatings only and **24** tons per day from thinning/cleanup/additives, for a total of **119** tons per day, on an annual average basis. The **95** tons per day from coatings represent about **8%** of the total stationary and area source VOC emissions, and about **4%** of all VOC emissions statewide. Control of emissions from architectural coatings is primarily the responsibility of the local Air Pollution Control Districts and Air Quality Management Districts (Districts.) To assist Districts in reducing emissions from this source, ARB approved a Suggested Control Measure for Architectural Coatings (SCM) in 1977, and amended it in 1985, 1989, and 2000. These SCMs have been used as models for Districts when adopting and amending their local rules. As of January 2007, **20** local air districts have adopted the architectural coating limits from the 2000 SCM.

During the June 2000 Board hearing, Board members approved the 2000 SCM and adopted Resolution 00-23. This Resolution directed the ARB staff to work with industry and other stakeholders in assessing the ozone-forming potential (i.e., reactivity) of architectural coatings, and to evaluate the feasibility of developing a reactivity-based control strategy. In June 2001, December 2002, and January 2004, ARB staff provided updates to the Board, regarding progress in implementing Resolution 00-23 (ARB, 2001; ARB, 2002; ARB, 2004.) This progress is summarized below:

Reactivity Evaluation Tasks	**ARB Accomplishments**
• Assess the reactivity of individual VOC species in consideration of the best available science.	• ARB funded a $300,000 research project with the University of California, Riverside to assess the reactivity of key solvents in architectural coatings, including Texanol® and six hydrocarbon solvents. The final report for this project was completed in March 2005.
• Conduct a comprehensive survey of the architectural coatings industry.	• In 2001 and 2005, ARB conducted architectural coatings surveys. Results from these surveys are summarized in the “2001 Architectural Coatings Survey, Final Report, October 2003” and the “2005 Architectural Coatings Survey, Draft Report, September 2006”.
• Assess the extent to which VOCs emitted from architectural coatings contribute to ozone levels.	• ARB used data from the architectural coating surveys to estimate the potential amount of ozone that is generated by architectural coatings. The ozone estimates from the 2001 survey were contained in the “2001 Architectural Coatings Survey, Final Reactivity Analysis, March 2005”. The ozone estimates from the 2005 survey are summarized in Chapter 2 of this report.

ARB staff is continuing the investigation into the feasibility of a reactivity-based architectural coatings regulation, including consideration of the following advantages and disadvantages.

Advantages

- Reactivity-based regulations may provide opportunities to achieve greater ozone reductions, because it is becoming more difficult to achieve these reductions with traditional mass-based VOC limits.
- Reactivity-based regulations target VOCs with the greatest ozone forming potential, rather than treating all VOCs equally.
- Reformulation options may be greater with a reactivity-based strategy, because there is a wide range of VOC species, VOC contents, and alternative technologies available.

Disadvantages

- Compliance testing will require more resources and will be more complicated, because laboratory analysis will involve determining the identity and quantity of each VOC and exempt compound, unlike the current method which only determines the total amount of VOCs.
- Most of the architectural coating market is already waterborne and has a relatively low level of reactivity. Therefore, the opportunities for reformulation may be limited to a small number of categories that still have solventborne coatings.
- Some toxic compounds (e.g., methylene chloride and perchloroethylene) have a low reactivity, which could lead to increased usage in coatings that are subject to a reactivity-based limit. Therefore, the use of toxic chemicals would need to be controlled.

Reactivity can be characterized in a number of ways, using a variety of measurement scales, such as those developed by Dr. William Carter at the University of California, Riverside. Carter evaluated a variety of scales and concluded that the Maximum Incremental Reactivity (MIR) scale is the most appropriate for California (Carter, 1994.) The ARB uses the MIR scale for regulatory applications because it reflects reactivities under environmental conditions that are most sensitive to the effects of VOC controls, such as in the South Coast Air Basin.

The MIR scale can be used to assign reactivity values for most of the pure chemicals that are used in architectural coatings. However, hydrocarbon solvents are a major ingredient in architectural coatings and they generally consist of mixtures, rather than pure compounds. For hydrocarbon solvents, ARB developed a bin system in conjunction with the development of the Aerosol Coating regulation (ARB, 2000.) These bins assign MIR values, based on average boiling points and hydrocarbon characteristics (e.g., aromatic content).

MIR values and VOC emission quantities can be used to estimate the amount of ozone that could potentially be formed under MIR conditions (i.e., the maximum ozone formation potential). Estimating actual atmospheric ozone concentrations involves the use of complicated computer modeling programs that analyze emission data, meteorological data, MIR values, and other information. This type of modeling effort is outside the scope of this reactivity analysis. For the purposes of this report, we use the maximum ozone formation potential to provide a comparison of the relative contributions from different coating categories and identify categories that may be candidates for achieving additional ozone reductions.

After determining the maximum ozone formation potential, it is necessary to normalize the values in a way that allows comparison between the different coating categories. In this report we considered the following possible approaches:

- Maximum Ozone Per Pound of Coating
- Maximum Ozone Per Gallon of Coating
- Maximum Ozone Per Pound of Solids
- Maximum Ozone Per Gallon of Solids

Table E-1 contains a summary of maximum potential ozone quantities under MIR conditions. The table also contains the maximum potential ozone per gallon of coating. As shown below, the amount of potential ozone generated by each gallon of solventborne coating is generally higher than the amount generated by each gallon of waterborne coating. However, the overall quantity of maximum potential ozone (tons/day) is sometimes higher in the waterborne column, because waterborne coatings dominate the architectural coating market.

Table E-1: ***Maximum Ozone Formation Potential***

Coating Category	Maximum Ozone (tons/day)			[Maximum Ozone, lbs] per [Gallon Coating]		
	SB	WB	All	SB	WB	All
Bituminous Roof	1.48	0.07	1.55	4.80	0.04	0.73
Bituminous Roof Primer	0.48	0.02	0.50	5.88	1.67	5.38
Bond Breakers	0.01	0.75	0.77	10.80	2.94	2.97
Clear Brushing Lacquer	1.06	0.00	1.06	11.16	NA	11.16
Concrete Curing Compounds	0.72	1.00	1.73	12.09	0.86	1.41
Driveway Sealer	0.04	0.04	0.08	6.68	0.01	0.03
Dry Fog	1.51	0.21	1.72	5.90	0.79	3.32
Faux Finishing	0.03	0.94	0.97	4.71	2.29	2.32
Fire Resistive	0.04	0.00	0.04	6.06	0.19	2.56
Fire Retardant - Clear	0.02	0.00	0.02	19.58	NA	19.58
Fire Retardant - Opaque	0.90	0.00	0.91	3.65	0.15	3.31
Flat	0.10	36.61	36.72	18.06	0.72	0.72
Floor	1.30	5.37	6.66	7.40	3.20	3.60
Form Release Compounds	1.29	0.03	1.32	3.32	0.50	2.98
Graphic Arts	0.02	0.00	0.02	4.28	2.39	3.92
High Temperature	0.14	0.00	0.14	8.66	NA	8.66
Industrial Maintenance	13.21	1.66	14.87	6.99	1.76	5.24
Lacquers	8.51	0.74	9.25	6.62	1.53	5.23
Low Solids	0.00	0.10	0.10	NA	1.17	1.17
Magnesite Cement	0.72	0.00	0.72	20.12	NA	20.12

Table E-1: ***Maximum Ozone Formation Potential***

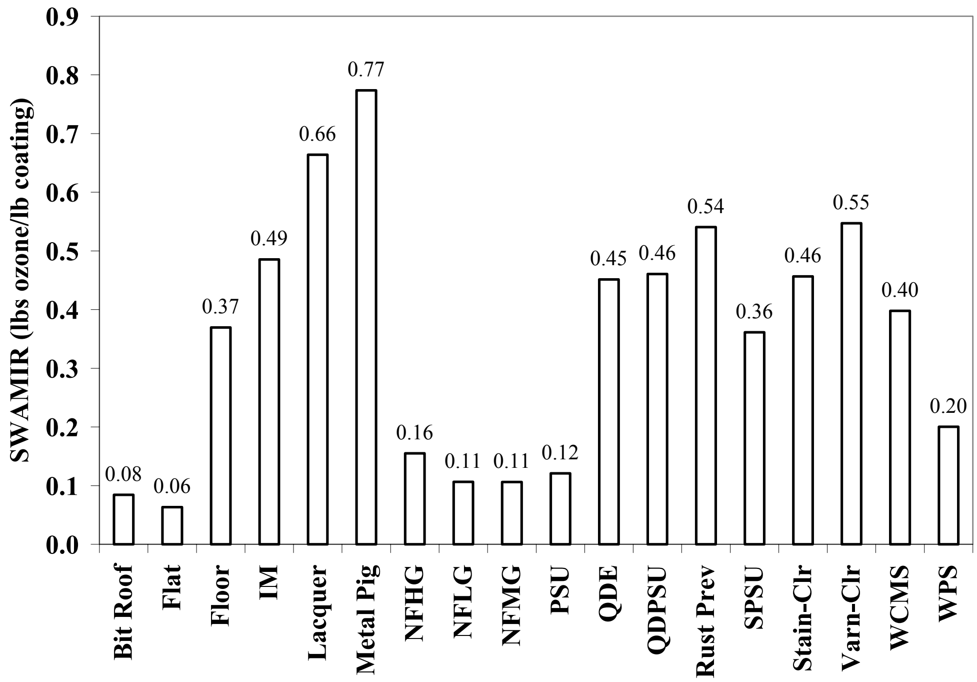
Coating Category	Maximum Ozone (tons/day)			[Maximum Ozone, lbs] per [Gallon Coating]		
	SB	WB	All	SB	WB	All
Mastic Texture	0.27	0.86	1.13	1.64	0.90	1.01
Metallic Pigmented	5.79	0.25	6.05	8.21	1.40	6.82
Multi-Color	0.00	0.01	0.01	5.69	0.31	0.42
Nonflat - High Gloss	0.27	3.54	3.81	4.84	1.50	1.58
Nonflat - Low Gloss	0.03	18.56	18.59	4.73	1.13	1.13
Nonflat - Medium Gloss	0.46	29.18	29.64	4.31	1.07	1.08
Other	0.07	0.01	0.08	18.95	0.09	0.62
Pre-Treatment Wash Primer	0.02	0.01	0.03	13.42	1.04	3.41
Primer, Sealer, and Undercoater	1.22	17.16	18.38	3.97	1.23	1.29
Quick Dry Enamel	4.45	0.17	4.61	4.55	2.44	4.41
Quick Dry Primer, Sealer, and Undercoater	1.69	0.01	1.69	5.58	0.15	4.94
Roof	0.47	0.72	1.19	7.85	0.38	0.61
Rust Preventative	15.32	0.20	15.52	5.58	1.63	5.41
Sanding Sealers	0.50	0.04	0.53	5.99	1.17	4.62
Shellacs - Clear	0.55	0.00	0.55	7.66	NA	7.66
Shellacs - Opaque	1.28	0.00	1.28	6.40	NA	6.40
Specialty Primer, Sealer, and Undercoater	11.09	0.56	11.64	5.28	0.85	4.23
Stains - Clear/Semitransparent	8.11	0.70	8.82	4.05	1.34	3.49
Stains - Opaque	0.15	1.22	1.37	5.38	0.96	1.05
Swimming Pool	0.08	0.01	0.10	12.02	3.58	8.87
Swimming Pool Repair and Maintenance	0.11	0.00	0.11	36.41	NA	36.41
Traffic Marking	2.35	1.90	4.24	5.20	0.74	1.40
Varnishes - Clear	4.70	0.84	5.54	4.95	2.21	4.17
Varnishes - Semitransparent	0.42	0.02	0.44	3.57	1.49	3.38
Waterproofing Concrete/Masonry Sealers	7.18	1.17	8.35	5.64	1.36	3.92
Waterproofing Sealers	1.32	2.06	3.38	4.74	1.16	1.65
Wood Preservatives	0.95	0.01	0.96	4.21	1.07	4.04
TOTALS:	**100.4**	**126.8**	**227.2**	**5.55**	**0.95**	**1.50**

Notes:
NA = Not Applicable. No sales were reported for this subcategory.

Sales-weighted average MIR values (SWAMIRs) provide another way to characterize the overall reactivity of a given category. Sales-weighting assigns greater importance to products that have higher sales volumes. Therefore, if a category has a particularly dominant product, the SWAMIR for that category will be more reflective of the dominant product.

Figure E-1 contains SWAMIRs for selected coating categories. Data are provided in units of [Lb Ozone/Lb Coating], which corresponds to the approach that ARB used in the reactivity-based Aerosol Coatings regulation.

Figure E-1
Sales-Weighted Average MIR – [Lb Ozone/Lb Coating]

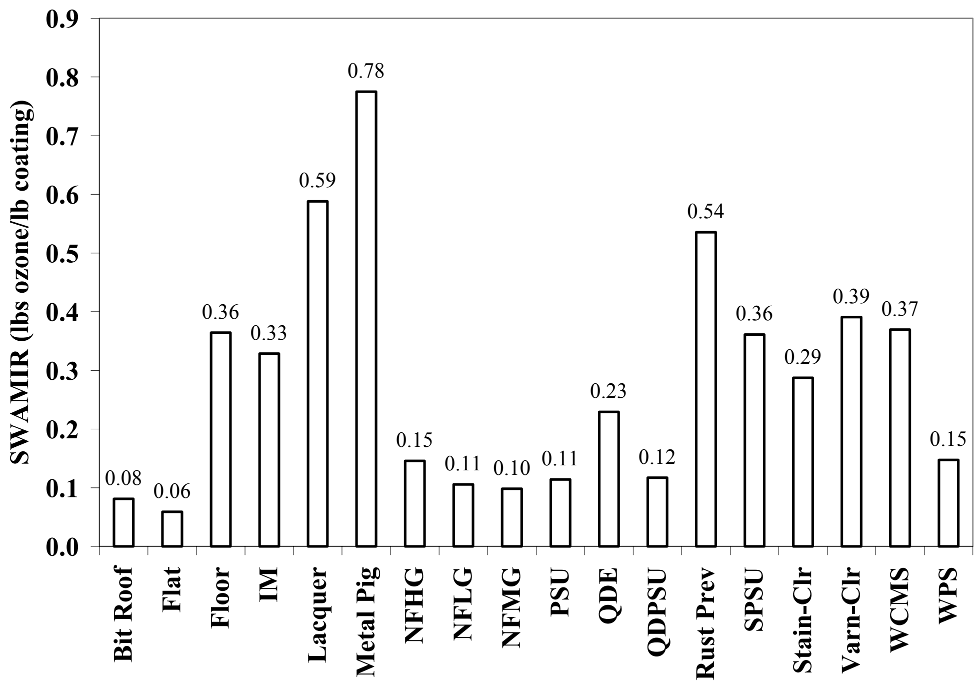


Notes:
1. [Lb Ozone]/[Lb Coating] = [Maximum Ozone Formation Potential]/[Total Coating Mass]
2. [Maximum Ozone Formation Potential] = ∑ [Ingredient Emissions, lbs]*[MIR, g Ozone/g Ingredient]
3. [Total Coating Mass] = ∑ [Coating Sales Volume, gals]*[Coating Density, lb/gal]
4. This figure includes data from small containers (1 quart or less).
5. This figure includes ozone generated from all volatile emissions, including VOCs and exempt compounds.
6. Bit Roof = Bituminous Roof; IM = Industrial Maintenance; Metal Pig = Metallic Pigmented; NFHG = Nonflat – High Gloss; NFLG = Nonflat – Low Gloss; NFMG = Nonflat – Medium Gloss; PSU = Primer, Sealer, Undercoater; QDPSU = Quick Dry Primer, Sealer, Undercoater; Rust Prev = Rust Preventative; Stain – Clr = Stains – Clear/Semitransparent; Varn – Clr = Varnishes – Clear; WCMS = Waterproofing Concrete/Masonry Sealers; WPS = Waterproofing Sealers.

Detailed SWAMIR data for all coating categories are contained in Appendix B, including a breakdown for solventborne and waterborne formulations. Appendix B also contains SWAMIRs for compliant and non-compliant coatings, based on the VOC limits contained in ARB's 2000 Architectural Coatings SCM and the SCAQMD VOC limits that will take effect in or before 2008.

Figure E-2 contains data similar to Figure E-1, but it provides SWAMIRs only for those reported coatings that complied with the VOC limits in ARB's 2000 Suggested Control Measure. In addition, Figure E-2 does not include sales of small containers (one quart or less), because they are exempt from the SCM VOC limits. When comparing Figure E-1 (all coatings) to Figure E-2 (compliant coatings only), the SWAMIRs are similar for most of the categories. However, the SWAMIRs on Figure E-2 are significantly lower for compliant coatings in the following categories: Industrial Maintenance; Quick Dry Enamel; Quick Dry Primer, Sealer, Undercoater; Stains – Clear/Semitransparent; and Varnishes - Clear.

Figure E-2
Sales-Weighted Average MIR – [Lb Ozone/Lb Coating]
(Only Includes Compliant Coatings in Large Containers)



Notes:
1. [Lb Ozone]/[Lb Coating] = [Maximum Ozone Formation Potential]/[Total Coating Mass]
2. [Maximum Ozone Formation Potential] = ∑ [Ingredient Emissions, lbs]*[MIR, g Ozone/g Ingredient]
3. [Total Coating Mass] = ∑ [Coating Sales Volume, gals]*[Coating Density, lb/gal]
4. This figure only includes data for coatings that comply with the VOC limits in the 2000 SCM.
5. This figure does not include data from small containers (1 quart or less).
6. This figure includes ozone generated from all volatile emissions, including VOCs and exempt compounds.

To identify opportunities for ozone reductions, it is important to know which ingredients contribute the most to a category's potential ozone creation. The following table focuses on the ingredients that are the primary contributors to either VOC emissions or maximum potential ozone totals for selected categories. Table E-2 only lists ingredients that represent more than 10% of the total maximum potential ozone for a category or ingredients that represent more than 10% by weight of the total volatile ingredients (excluding water). It highlights categories where it may be possible to replace a more reactive ingredient with one that is less reactive.

Table E-2: ***Ingredients That Contribute the Most to Emissions and Potential Ozone***

Category	CAS	Ingredient	MIR (g O^3/ g ingr)	Ingred. Qty. (tpd)	Max. Ozone (tpd)	% of Total Volatiles For Category	% of Total Max. Ozone From Category
Bituminous Roof		Bin 15 Hydrocarbon Solvent	1.82	0.53	0.96	81%	62%
		Bin 22 Hydrocarbon Solvent	7.51	0.06	0.44	9%	29%
Flat	107211	Ethylene Glycol	3.63	3.48	12.65	25%	34%
	124685	2-Amino-2-Methyl-1-Propanol	15.08	0.61	9.19	4%	25%
	25265774	2,2,4-Trimethyl-1,3-Pentanediol Isobutyrate	0.89	6.46	5.75	47%	16%
	57556	Propylene Glycol	2.75	1.84	5.05	13%	14%
Floor	9986	Unknown	2.73	1.36	3.72	60%	56%
		Bin 22 Hydrocarbon Solvent	7.51	0.12	0.88	5%	13%
	29911271	Dipropylene Glycol Monopropyl Ether	2.13	0.24	0.51	11%	8%
Industrial Maintenance	1330207	Xylene	7.48	0.67	5.01	15%	34%
		Bin 11 Hydrocarbon Solvent	0.91	0.59	0.54	14%	4%
Lacquers	67641	Acetone	0.43	4.02	1.73	55%	19%
	1330207	Xylene	7.48	0.18	1.34	2%	15%
	111762	2-Butoxy Ethanol	2.90	0.33	0.94	4%	10%
	123864	Butyl Acetate, 1-	0.89	0.87	0.78	12%	8%
Metallic Pigmented		Bin 15 Hydrocarbon Solvent	1.82	1.35	2.45	62%	41%
		Bin 22 Hydrocarbon Solvent	7.51	0.32	2.43	15%	40%
Nonflat - High Gloss	107211	Ethylene Glycol	3.63	0.35	1.26	26%	33%
	124685	2-Amino-2-Methyl-1-Propanol	15.08	0.05	0.79	4%	21%
	57556	Propylene Glycol	2.75	0.17	0.48	13%	13%
	5444757	2-Ethylhexyl Benzoate	2.73	0.17	0.46	13%	12%
	25265774	2,2,4-Trimethyl-1,3-Pentanediol Isobutyrate	0.89	0.33	0.30	25%	8%

Table E-2: *Ingredients That Contribute the Most to Emissions and Potential Ozone*

Category	CAS	Ingredient	MIR (g O^3/ g ingr)	Ingred. Qty. (tpd)	Max. Ozone (tpd)	% of Total Volatiles For Category	% of Total Max. Ozone From Category
Nonflat - Low Gloss	107211	Ethylene Glycol	3.63	2.61	9.47	39%	51%
	57556	Propylene Glycol	2.75	0.93	2.56	14%	14%
	124685	2-Amino-2-Methyl-1-Propanol	15.08	0.15	2.26	2%	12%
	25265774	2,2,4-Trimethyl-1,3-Pentanediol Isobutyrate	0.89	1.94	1.72	29%	9%
Nonflat - Medium Gloss	107211	Ethylene Glycol	3.63	3.31	12.02	28%	41%
	57556	Propylene Glycol	2.75	2.70	7.41	23%	25%
	25265774	2,2,4-Trimethyl-1,3-Pentanediol Isobutyrate	0.89	3.83	3.41	33%	12%
Primer, Sealer, and Undercoater	107211	Ethylene Glycol	3.63	2.59	9.41	40%	51%
	124685	2-Amino-2-Methyl-1-Propanol	15.08	0.24	3.68	4%	20%
	25265774	2,2,4-Trimethyl-1,3-Pentanediol Isobutyrate	0.89	1.67	1.48	26%	8%
		Bin 11 Hydrocarbon Solvent	0.91	0.76	0.69	12%	4%
Quick Dry Enamel		Bin 11 Hydrocarbon Solvent	0.91	2.33	2.12	72%	46%
		Bin 10 Hydrocarbon Solvent	2.03	0.34	0.70	11%	15%
Quick Dry Primer, Sealer, and Undercoater		Bin 6 Hydrocarbon Solvent	1.41	0.63	0.89	62%	53%
		Bin 11 Hydrocarbon Solvent	0.91	0.22	0.20	22%	12%
Rust Preventative		Bin 10 Hydrocarbon Solvent	2.03	1.87	3.79	21%	24%
		Bin 11 Hydrocarbon Solvent	0.91	3.86	3.51	44%	23%
		Bin 15 Hydrocarbon Solvent	1.82	1.21	2.20	14%	14%
	1330207	Xylene	7.48	0.25	1.88	3%	12%
Specialty Primer, Sealer, and Undercoater		Bin 22 Hydrocarbon Solvent	7.51	0.62	4.66	10%	40%
		Bin 11 Hydrocarbon Solvent	0.91	4.45	4.05	74%	35%
Stains - Clear/ Semitransparent		Bin 11 Hydrocarbon Solvent	0.91	3.87	3.52	59%	40%
Varnishes - Clear		Bin 11 Hydrocarbon Solvent	0.91	2.77	2.52	70%	46%
		Bin 15 Hydrocarbon Solvent	1.82	0.41	0.75	10%	14%

Table E-2: ***Ingredients That Contribute the Most to Emissions and Potential Ozone***

Category	CAS	Ingredient	MIR (g O^3/ g ingr)	Ingred. Qty. (tpd)	Max. Ozone (tpd)	% of Total Volatiles For Category	% of Total Max. Ozone From Category
Waterproofing Concrete/Masonry Sealers		Bin 22 Hydrocarbon Solvent	7.51	0.42	3.12	11%	37%
		Bin 6 Hydrocarbon Solvent	1.41	0.65	0.92	17%	11%
	67641	Acetone	0.43	0.55	0.24	14%	3%
	98566	4-Chlorobenzotrifluoride	0.11	0.58	0.06	15%	1%
Waterproofing Sealers		Bin 11 Hydrocarbon Solvent	0.91	0.61	0.55	39%	16%
	34590948	Dipropylene Glycol Methyl Ether	2.46	0.18	0.45	12%	13%
	107211	Ethylene Glycol	3.63	0.12	0.43	7%	13%

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Chapter 1 -- Introduction and Background

In April 2005, the Air Resources Board (ARB or Board) conducted a survey of companies that sold architectural coating products in California in 2004. The survey gathered detailed ingredient information for the volatile compounds contained in each coating product (ARB, 2006.) ARB staff used these ingredient data to analyze the photochemical reactivity (i.e., ozone-forming potential) associated with architectural coatings. This document is intended to provide different options for evaluating the reactivity of architectural coatings, but it is not a formal regulatory document.

When coatings are applied, they release different types of organic compounds that can react in the atmosphere to produce different amounts of ozone. This ozone forming potential is called hydrocarbon reactivity and it is determined by the photochemical reactions in the atmosphere. If a coating contains a small amount of a highly reactive compound, it could have a relatively high reactivity rating even if it has a low level of volatile organic compounds (VOCs). Similarly, a coating that has a high VOC content may have a relatively low reactivity rating, if it contains compounds that aren't very reactive. The following sections contain a detailed description of the chemical reactions that lead to the formation of ozone in the atmosphere.

Section 1.1. Chemistry of Ozone Formation and Reactivity

Tropospheric chemical generation of ozone involves complex interactions among hydrocarbons and oxides of nitrogen (NO_x) under sunlight (Bergin, 1998; Carter, 1994; NRC, 1991; NRC, 1999; Silman, 1995.) In the ambient air, the primary process leading to ozone formation is the photolysis of nitrogen dioxide (NO_2).

$$NO_2 + h\nu \rightarrow NO + O(^3P)$$

$$O(^3P) + O_2 + M \rightarrow O_3 + M$$

where
NO_2 = Nitrogen Dioxide
$h\nu$ = Ultraviolet Light
NO = Nitric Oxide
M = A third body, such as N_2
$O(^3P)$ = A ground state oxygen atom
O_2 = Oxygen
O_3 = Ozone

At photo-equilibrium, the steady state ozone concentration is then given by

$$[O_3]_{steady} = \frac{k_{photo}[NO_2]}{k_1[NO]}$$

where
k_{photo} = the photolysis rate of NO_2
k_1 = the rate constant for the reaction of NO with O_3

It is apparent from this equation that additional processes converting NO to NO_2 can lead to enhanced ozone levels. VOCs are chemicals known to play an important role in such processes (NRC, 1991.) The ability of a VOC to induce ozone formation is known as "reactivity." Under ambient atmospheric conditions, the major reactions involving VOCs can be summarized as follows:

$$VOC + OH \rightarrow RO_2 + \text{products}$$

$$RO_2 + \alpha NO \rightarrow \beta NO_2 + \text{radicals}$$

$$\text{Radicals} \rightarrow \delta OH + \text{products (e.g., HCHO)}$$

The reaction is initiated by hydroxyl (OH) radicals reacting to form peroxy radicals (RO_2). In the presence of sufficient amounts of NO_x (i.e., NO and NO_2), reactions of peroxy radicals with NO compete effectively with their reactions with other peroxy radicals. This, in turn, leads to NO-to-NO_2 conversions and ultimately results in regeneration of the OH radicals. Therefore, a VOC can enhance the rate of ozone formation via an increase in the amount of NO_2 (β) converted from NO. In addition, the reaction with OH radicals is the major (or in most cases the only) reaction for most VOCs. Therefore, any enhanced production of OH radicals ($\delta > 1$), either by the parent VOC or its products (e.g., formaldehyde (HCHO)), would increase not only its own rate of ozone formation but also increase the rate of ozone formation of other VOCs present.

However, if a radical termination process is present in the VOC's reactions, it will decrease the amount of other VOCs reacting. This affects the total amount of O_3 formed (Bergin, 1998; Carter, 1994.) Furthermore, processes like organic nitrate formation (e.g., peroxyacetyl nitrate (PAN) from acetaldehyde) can affect the ability of a VOC to form ozone by reducing the amount of NO available (α) to form NO_2 (Atkinson, 1994.)

Hence, the impact of a VOC on ozone formation is a function of:

(1) its reaction rates (i.e., kinetics);
(2) direct mechanistic effects such as the amount of NO-to-NO_2 conversion;
(3) indirect mechanistic effects on other VOCs via processes such as radical initiation; and
(4) the presence of other species in an urban airshed with which the VOCs could potentially react.

Consequently, there is a wide variation in the ability of VOCs to induce ozone formation, and the relative importance of these processes determines whether a VOC has an enhancing (i.e., positive reactivity) or a suppressing effect (i.e., negative reactivity) on ozone formation.

Section 1.2 ARB Reactivity-Based Regulations

The ARB has pioneered the use of reactivity in regulations controlling VOC emissions. In 1991, the Board approved the Low Emission Vehicles and Clean Fuels regulation that allowed for the use of reactivity adjustment factors (ARB, 1990.) In June 2000, the Board approved a reactivity-based regulation for aerosol coatings, based on the Maximum Incremental Reactivity (MIR) scale (ARB, 2000.) ARB's Aerosol Coating Regulation is provided in Appendix A. This regulation was approved by the United States Environmental Protection Agency (U.S. EPA) in 2005 (U.S. EPA, 2005.)

Section 1.3 Federal Policy on Reactivity-Based Regulations

In 2005, the U.S. EPA published a guidance document regarding the use of innovative reactivity-based approaches to achieve ozone reduction (U.S. EPA, 2005a.) This guidance encourages states to consider photochemical reactivity when developing control measures for state implementation plans (SIPs). U.S. EPA provided the following ways that reactivity could be addressed during the SIP development process:

- Develop speciated emission inventories to help identify the most reactive VOCs.
- Prioritize control measures based on reactivity.
- Target emissions of highly reactive VOCs with specific control measures.
- Encourage VOC substitution using reactivity-weighted emission limits.

U.S. EPA's guidance document supports the approach in ARB's Aerosol Coatings Regulation, which establishes reactivity limits based on individual ingredients rather than total VOC mass-based limits.

Section 1.4 ARB Suggested Control Measure for Architectural Coatings

Architectural coatings are a large source of VOC emissions. Except for consumer products, it is the largest single source of VOC emissions among all stationary and area sources. In 2004, architectural coatings and associated solvents emitted approximately **95** tons per day from coatings only and **24** tons per day from thinning/cleanup/additives, for a total of **119** tons per day, on an annual average basis. The **95** tons per day from coatings represent about **8%** of the total stationary and area source VOC emissions, and about **4%** of all VOC emissions statewide. Control of emissions from architectural coatings is primarily the responsibility of the local Air Pollution Control Districts and Air Quality Management Districts. To assist Districts in reducing emissions from this source, ARB approved a Suggested Control Measure for Architectural Coatings (SCM) in 1977, and amended it in 1985, 1989, and 2000. These SCMs have been used as models for Districts when adopting and amending their local rules. As of January 2007, **20** local air districts have adopted the architectural coating limits from the 2000 SCM.

During the June 2000 Board hearing, Board members approved the latest SCM update and adopted Resolution 00-23. This Resolution directed the ARB staff to work with industry and other stakeholders in assessing the ozone-forming potential (i.e., reactivity) of architectural coatings, and to evaluate the feasibility of developing a reactivity-based control strategy. This evaluation is to include:

(1) assessing the reactivity of individual VOC species in consideration of the best available science;
(2) conducting a comprehensive survey of the architectural coatings industry; and
(3) assessing the extent to which VOCs emitted from architectural coatings contribute to ozone levels.

Testimony at the June 2000 hearing underscored industry's interest in reactivity-based limits and suggested that improved science is a prerequisite to developing reactivity-based limits.

In June 2001, December 2002, and January 2004, ARB staff provided updates to the Board, regarding progress in implementing Resolution 00-23 (ARB, 2001; ARB, 2002; ARB, 2004.) A brief summary of ARB's progress is provided below:

(1) ARB funded a $300,000 research project with the University of California, Riverside that included conducting chamber experiments to verify the chemical mechanisms used to identify the maximum incremental reactivities for some key solvents in architectural coatings. These solvents included Texanol® and six hydrocarbon solvents. The final report for this project was completed in March 2005.
(2) In 2001 and 2005, ARB conducted comprehensive surveys of the architectural coatings industry. Results from these surveys are summarized in the "2001 Architectural Coatings Survey, Final Report, October 2003" and the "2005 Architectural Coatings Survey, Draft Report, September 2006".
(3) ARB used the data from these surveys to estimate the reactivity of architectural coatings. The results from the 2001 survey were contained in the "2001 Architectural Coatings Survey, Final Reactivity Analysis, March 2005". The results from the 2005 survey are summarized in Chapter 2 of this report. The extent to which architectural coatings contribute to ozone levels can be evaluated in a variety of ways. To actually estimate ozone concentrations, it is necessary to conduct detailed air dispersion modeling calculations. Another method for characterizing the relative ozone impacts is to identify the maximum ozone forming potential under MIR conditions. For the purposes of this report, we have chosen the latter approach, because it is a much simpler analysis that still provides a method of comparing relative ozone impacts for different coatings.

ARB staff is continuing the investigation into the feasibility of a reactivity-based architectural coatings regulation, including consideration of the following advantages and disadvantages.

Section 1.5 Advantages of a Reactivity-Based SCM for Architectural Coatings

There are several advantages associated with a reactivity-based control strategy for architectural coatings. Many of the elements of a successful reactivity program are met with architectural coatings. Architectural coatings are a discrete and well-defined emissions source category, which is regularly updated with industry surveys. The reactivities of many VOC ingredients used in architectural coatings are already well characterized. Several manufacturers have expressed an interest in working with ARB on a reactivity-based SCM.

The use of mass-based VOC limits has resulted in significant emission reductions for architectural coatings. However, mass-based emission reductions are becoming more difficult to achieve as VOC limits decline and water-borne coatings increasingly dominate the market (more than 80 percent of the architectural coatings sold are water-borne products). Thus, reactivity-based limits offer a new opportunity to achieve additional ozone reductions. We expect an equal or greater air quality benefit compared to a mass-based strategy, because VOCs with the greatest ozone forming potential will be targeted rather than treating all VOCs equally.

Another potential advantage involves the use of exempt compounds. Under a reactivity-based approach, the reactivity of exempt compounds would be included when evaluating the overall reactivity of a coating product. With the current mass-based approach, exempt compounds are completely excluded when determining the VOC level. Theoretically, the use of exempt compounds could increase substantially to meet VOC levels and there would be a non-negligible ozone impact associated with the increased use of exempt compounds. This issue would not be a concern with reactivity-based limits.

The reformulation options may be greater with a reactivity-based strategy, because there is a wide range of VOC species, VOC contents, and alternative technologies available. At the same time, there should be less of a tendency for lower reactive solvents to be replaced with higher reactive or toxic solvents to lower the total VOC content. For example, we would expect to see a decreased use of some toxic compounds, such as xylene and toluene, because of their high reactivity.

There are also advantages associated with enforceability. If reactivity-based limits were developed in the same manner as was done for the Aerosol Coatings Regulation, there would no longer be a need to consider U.S. EPA's and ARB's exempt VOCs based on negligible reactivity, since the reactivity of all VOCs would be counted and nothing would be exempt. Depending on how the reactivity-based limit is defined, the "less water and exempts" calculation for determining the VOC content may cease to be an issue, since limits may be expressed in units other than grams of VOC per liter of coating, less water and exempt compounds.

Section 1.6 Disadvantages of a Reactivity-Based SCM for Architectural Coatings

There are implications for both the regulatory agencies and the manufacturers if we go forward with a reactivity-based SCM for architectural coatings. Architectural coatings are regulated by the local air districts. Since the districts may be implementing a more complex reactivity-based regulation, the ARB will provide assistance as needed. Therefore, this would result in increased resource needs for the local districts and ARB.

Compliance determination under a reactivity-based program differs from that under a traditional mass-based program. The identity and quantity of each VOC and exempt compound in a coating is needed to determine compliance with a reactivity-based limit. This may involve multiple gas chromatography with mass spectrometry (GC/MS) runs. Many districts may need ARB assistance with this type of analysis. This again would result in the need for increased resources.

To verify compliance with a reactivity-based limit, districts would require manufacturers to divulge the individual VOC ingredients in their coatings. As allowed under the Federal Clean Air Act, this emissions-related data could also be released to the public, if requested. Under such a scheme, manufacturers may be concerned about maintaining the confidentially of their product formulas. One option would be that only the reactive, volatile components of the coating would need to be divulged and the non-reactive components such as solids or resins could be lumped together to maintain product confidentially. Such an agreement was reached between the aerosol coatings industry and ARB for the aerosol coatings reactivity-based regulation.

Since more than 80 percent of the market is already water-borne, and relatively low reactive mineral spirits dominate the VOCs in solvent-borne coatings, there may be challenges to reformulating with lower-reactive solvents. In addition, we will need to analyze whether acceptable substitutes are available for the highly reactive solvents used in architectural coatings, if mandatory reactivity-based limits are proposed. This analysis will need to examine technical feasibility, economic impacts, and potential health effects.

Any reactivity-based strategy would evaluate the potential uses of toxic compounds. Some toxic compounds (e.g., methylene chloride and perchloroethylene) have a low reactivity, which could lead to increased usage in coatings that are subject to a reactivity-based limit. Therefore, it may be necessary to cap current uses and potentially prevent or minimize new uses of these toxic chemicals.

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Chapter 2 – Reactivity Analysis of Survey Data

Section 2.1 Individual MIR Values

Ozone is created by chemical reactions that occur between organic compounds and nitrogen oxides (NOx), in the presence of sunlight (see Chapter 1). The reactivity of organic compounds varies widely, depending on the specific chemical and the atmospheric conditions. Incremental reactivity is the change in ozone that is caused by adding a small amount of an organic compound to a standard gas mixture. This reactivity can be characterized in a number of ways, using a variety of measurement scales, such as those developed by Dr. William Carter at the University of California, Riverside:

MIR - Maximum Incremental Reactivity

> The MIR scale is based on a scenario derived by adjusting the NOx emissions in a base case scenario to yield the highest incremental reactivity of the Base Case Reactive Organic Gas (ROG) Mixture.[1]
>
> The MIR is the incremental reactivity computed for conditions in which the NO_x concentration would maximize the VOC reactivity. This scenario is typical in air parcels of low VOC-to-NO_x ratios, or air parcels in which ozone is most sensitive to VOC changes. These are typical of urban centers where there are high emissions of NO_x and the atmospheric chemistry is VOC-limited.
>
> MIR values are calculated from a computer box model that is based on the SAPRC chemical mechanism. Environmental chamber experiments have been conducted to verify and refine the SAPRC mechanism. Additional chamber experiments are ongoing and the mechanism is updated accordingly as new data are gathered.

MOIR - Maximum Ozone Incremental Reactivity

> The MOIR scale is based on a scenario derived by adjusting the NOx emissions in a base case scenario to yield the highest peak ozone concentration.
>
> The MOIR is the incremental reactivity computed for conditions that maximize the ozone concentration. The scenario is characterized by moderate VOC-to-NO_x ratios such that the highest ozone concentration is formed. These moderate VOC-to-NO_x ratios are generally encountered as the chemistry is in transition between VOC and NO_x limitations. In this scenario, ozone formation is relatively insensitive to concentrations of VOCs and NO_x, compared to its sensitivity to VOC control in the VOC-limited region and its sensitivity to NO_x control in the

[1] The Base Case ROG mixture is a mixture of reactive organic gases that represents the chemical composition of the air in 39 urban areas throughout the United States. The U.S. Environmental Protection Agency selected a high ozone episode from each of these 39 areas to establish a geographically representative distribution of conditions in ozone nonattainment areas.

NO_x-limited region. The ozone sensitivity to the VOC is studied after the NO_x concentrations are optimized to yield the maximum ozone concentration.

EBIR - Equal Benefit Incremental Reactivity

The EBIR scale is based on a scenario derived by adjusting the NOx emissions in a base case scenario so VOC and NOx reductions are equally effective in reducing ozone.

The EBIR is the incremental reactivity computed for conditions in which ozone sensitivity to VOC is equal to that of NO_x. The scenario is characterized by higher VOC-to-NO_x ratios such that VOC and NO_x controls are equally effective in reducing ozone.

Carter evaluated each of these three scales and concluded that, if only one scale is to be used for regulatory purposes, the MIR scale is the most appropriate for California (Carter, 1994.)

Although the MOIR is computed for conditions that maximize the ozone concentration, the MOIR and EBIR are more representative of lower NO_x and higher VOC conditions. In the grid modeling study conducted by McNair et al., a 3-D model was applied to a 3-day pollution episode in the Los Angeles Air Basin (McNair, 1992.) The results showed that the MIRs derived from the box models did not perform well in predicting peak ozone sensitivities to individual VOCs, but performed reasonably well in predicting the effects of the VOCs on the integrated exposure to ozone over the air quality standard. The MOIR scale did not compare as well as the MIR scale to either the peak ozone concentration or ozone exposure concentrations greater than the air quality standard. In another study, Bergin et al. conducted a more direct comparison with the MIR and MOIR scales (Bergin, 1995; Bergin, 1998a.) The results showed that the metrics compared relatively better with the MIR scale than with the MOIR scale. The results suggest that the MIR scale is most appropriate in areas rich in NO_x, such as the urban areas in California that exceed ozone air quality standards. On the federal level, the U.S. Environmental Protection Agency coordinates the Reactivity Research Working Group that is working to improve the scientific basis for reactivity-related regulatory policies.

The ARB is using the MIR scale for regulatory applications because the MIR scale reflects reactivities under environmental conditions that are most sensitive to the effects of VOC controls, such as in the South Coast Air Basin. The scale would be most accurate for VOC-limited conditions, in which VOC controls would be most effective. The MIR scale was also found to correlate well to scales based on integrated ozone yields, even in lower NO_x scenarios (Carter, 1994; McNair, 1992; Bergin, 1995.) Moreover, the MIR scale tends to predict low reactivities for slowly reacting compounds. The wider range of incremental reactivities in the MIR scale allows better discrimination in a manufacturer’s selection of a less reactive compound to substitute for a more reactive compound.

MIR values have been assigned for hundreds of organic compounds, including both VOCs and exempt compounds. ARB uses the term Reactive Organic Gases (ROG) for VOCs only and the term Total Organic Gases (TOG) to include both VOCs and exempt compounds. MIR values are expressed in units of grams ozone per gram TOG (g O_3/g TOG) and these values are updated periodically by Carter (Carter, 2003.) At an Executive Officer hearing in December 2003, ARB approved a formal update of the Tables of MIR Values for the Aerosol Coatings Regulation and any other future reactivity regulations. This update became effective on July 7, 2004 (ARB, 2004; CCR, 2004.) For water and solid ingredients, ARB staff used an MIR value of zero.

The MIR scale can be used to assign reactivity values for most of the pure chemicals that are used in architectural coatings. However, hydrocarbon solvents are a major ingredient in architectural coatings and they generally consist of mixtures, rather than pure compounds. For hydrocarbon solvents, ARB developed a bin system in conjunction with the development of the Aerosol Coating Regulation (ARB, 2000.) These bins assign MIR values, based on average boiling points and hydrocarbon characteristics (e.g., aromatic content). The bins are similar to the categories contained in the following standards from the American Society for Testing and Materials (ASTM):

D 235: Mineral Spirits (Petroleum Spirits, Hydrocarbon Dry Cleaning Solvent)
D 3734: High-Flash Aromatic Naphthas
D 3735: VM&P Naphthas

ARB worked with paint manufacturers and solvent suppliers to identify the appropriate bin numbers for the hydrocarbon solvents that were reported in the 2005 Architectural Coatings Survey.

Dr. Carter's MIR scale and the ARB hydrocarbon solvent bins provided MIR values for **95** percent by weight of the organic compounds reported in the 2005 survey. For the remaining organic compounds, ARB calculated default MIR values that reflected sales-weighted averages of the MIRs that had been identified. Separate default MIR values were calculated for solventborne and waterborne coatings using the following types of compounds: exempt compounds; hydrocarbon solvents; and other organic compounds (non-exempt, non-hydrocarbon solvent.) These values are listed in Table 2-1.

Table 2-1: ***Default MIR Values***

Type of Compound	**Default MIR Values (g Ozone/g TOG)**	
	Solventborne	*Waterborne*
Exempt Compounds	0.36	0.43
Hydrocarbon Solvents	1.59	2.00
Other (non-exempt, non-hydrocarbon solvent VOCs)	3.86	2.73

Note: Default MIR values are sales-weighted averages, based on mass, for reported ingredients that had MIRs assigned by Dr. Carter.

Section 2.2 Maximum Ozone Formation Potential

MIR values and VOC emission quantities can be used to estimate the amount of ozone that could potentially be formed under MIR conditions (i.e., the maximum ozone formation potential). Since the goal of the architectural coatings regulations is ozone reduction, it is important to identify which products and categories may create the most ozone. Estimating actual atmospheric ozone concentrations involves the use of complicated computer modeling programs that analyze emission data, meteorological data, MIR values, and other information. This type of modeling effort is outside the scope of this reactivity analysis. For the purposes of this report, we use the maximum ozone formation potential to provide a comparison of the relative contributions from different coating categories and identify categories that may be candidates for achieving additional ozone reductions.

Emissions data can be converted to maximum ozone formation potentials by using the ingredient information collected in ARB's Architectural Coating Surveys. The surveys gather data on the weight percentages of each ingredient in each coating and the density of each coating. Using this information, we can determine the mass of each ingredient in each product. This mass can then be multiplied by the MIR value for each ingredient to yield the maximum ozone formation potential, as described in the following equations:

(1) Calculate the mass of each ingredient in each product:

$$[\text{Ingredient Mass, lbs}]_i = [\text{Sales, gals}]*[\text{Density, lbs/gal}]*[\text{Ingredient Weight \%}]_i$$

(2) Calculate the maximum potential ozone generated from each ingredient in each product:

$$[\text{Ozone from Ingredient, lbs}]_i = [\text{Ingredient Mass, lbs}]_i *[\text{MIR, gram Ozone/gram ingred.}]_i$$

Note: This value represents the maximum potential ozone that would be formed under MIR conditions.

(3) Add up the maximum potential ozone generated by all ingredients in all products:

$$[\text{Total Ozone, lbs}] = [\text{Ozone from Ingred., lbs}]_1 + [\text{Ozone from Ingred., lbs}]_2 + \ldots + [\text{Ozone from Ingred., lbs}]_n$$

where $[\text{Ingredient Mass}]_i$ = The amount of each ingredient "i" in each coating product, pounds
Sales = Sales of each coating product, gallons
Density = Density of each coating product, pounds/gallon
$[\text{Ingredient Weight \%}]_i$ = Weight percent of each ingredient "i" in each coating product
$[\text{MIR}]_i$ = the MIR of each ingredient "i" in each coating product, grams ozone/gram ingredient
(Note: For solids and water, the MIR is zero.)
$[\text{Ozone from Ingredient}]_i$ = the maximum potential amount of ozone generated under MIR conditions by each ingredient "i" in each coating product, pounds
n = the total number of ingredients in all coating products

Table 2-6 contains a summary of maximum potential ozone quantities under MIR conditions. The survey gathered data for more than **11,200** products and product groupings. For approximately **80** products (which accounted for only **0.2** percent of the total sales volume), no ingredient data were submitted. Therefore, it was not possible to identify individual MIRs for each ingredient in these products. As a result, the total maximum potential ozone quantity provided below is slightly less than it should be, because it doesn't include the contribution from the products with missing ingredient data.

Table 2-2: ***Maximum Ozone Formation Potential (Tons/Day)***

Coating Category	Solventborne	Waterborne	Overall
Bituminous Roof	1.48	0.07	1.55
Bituminous Roof Primer	0.48	0.02	0.50
Bond Breakers	0.01	0.75	0.76
Clear Brushing Lacquer	1.06	NA	1.06
Concrete Curing Compounds	0.72	1.00	1.73
Driveway Sealer	0.04	0.04	0.08
Dry Fog	1.51	0.21	1.72
Faux Finishing	0.03	0.94	0.97
Fire Resistive	0.04	0.00	0.04
Fire Retardant - Clear	0.02	NA	0.02
Fire Retardant - Opaque	0.90	0.00	0.91
Flat	0.10	36.61	36.72
Floor	1.30	5.37	6.66
Form Release Compounds	1.29	0.03	1.32
Graphic Arts	0.02	0.00	0.02
High Temperature	0.14	NA	0.14
Industrial Maintenance	13.21	1.65	14.86
Lacquers	8.51	0.74	9.25
Low Solids	NA	0.10	0.10
Magnesite Cement	0.72	NA	0.72
Mastic Texture	0.27	0.86	1.13
Metallic Pigmented	5.79	0.25	6.05
Multi-Color	0.00	0.01	0.01
Nonflat - High Gloss	0.27	3.55	3.82
Nonflat - Low Gloss	0.03	18.56	18.58
Nonflat - Medium Gloss	0.46	29.18	29.64
Other	0.07	0.01	0.08
Pre-Treatment Wash Primer	0.02	0.01	0.03
Primer, Sealer, and Undercoater	1.22	17.16	18.38
Quick Dry Enamel	4.45	0.17	4.61
Quick Dry Primer, Sealer, and Undercoater	1.69	0.01	1.69
Recycled	0	0	0
Roof	0.47	0.72	1.19
Rust Preventative	15.32	0.20	15.52
Sanding Sealers	0.50	0.04	0.53
Shellacs - Clear	0.55	NA	0.55
Shellacs - Opaque	1.28	NA	1.28
Specialty Primer, Sealer, and Undercoater	11.09	0.56	11.64
Stains - Clear/Semitransparent	8.11	0.70	8.82
Stains - Opaque	0.15	1.22	1.37
Swimming Pool	0.08	0.01	0.10

Table 2-2: ***Maximum Ozone Formation Potential (Tons/Day)***

Coating Category	Solventborne	Waterborne	Overall
Swimming Pool Repair and Maintenance	0.11	NA	0.11
Traffic Marking	2.35	1.90	4.24
Varnishes - Clear	4.70	0.84	5.54
Varnishes - Semitransparent	0.42	0.02	0.44
Waterproofing Concrete/Masonry Sealers	7.18	1.17	8.35
Waterproofing Sealers	1.32	2.06	3.38
Wood Preservatives	0.95	0.01	0.96
Totals:	**100.4**	**126.7**	**227.2**

Notes:
1. This table contains Maximum Potential Ozone formed under MIR conditions.
2. "NA": Not applicable, because no coating sales were reported in this subcategory.
3. For Recycled coatings, maximum potential ozone is zero because it is assumed that the ozone should be associated with the sales of the original product, prior to recycling.
4. This table includes data from small containers (1 quart or less).
5. This table includes ozone generated from all volatile emissions, including VOCs and exempt compounds.

The breakdown between solventborne and waterborne ozone is graphically illustrated in Figure 2-1. Solventborne coatings only account for 12% of the total coating sales in California, but they represent 44% of the potential ozone. This is due to the fact that solventborne coatings generally contain more pounds of VOC per gallon than waterborne coatings. Overall, this higher level of VOCs results in solventborne coatings generating more potential ozone per gallon than waterborne coatings.

Figure 2-1
Waterborne and Solventborne Maximum Potential Ozone

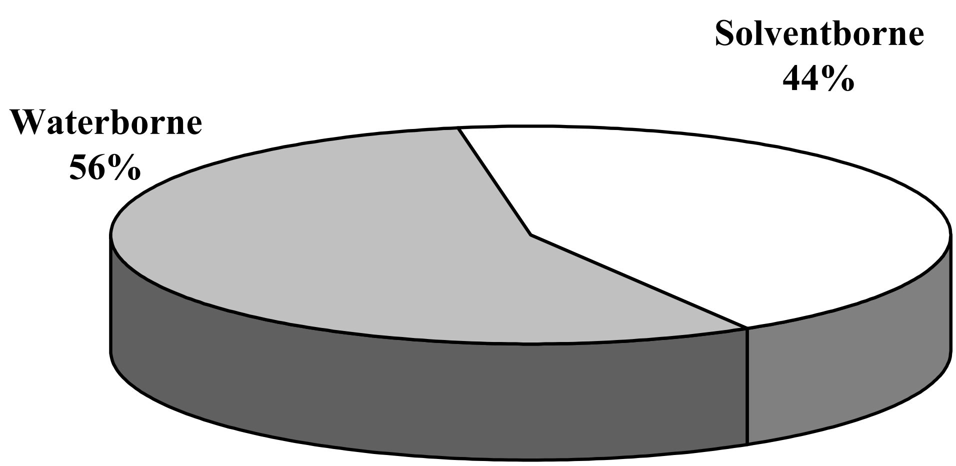


Figure 2-2 is a chart that highlights the top ten coating categories, based on maximum potential ozone formed under MIR conditions. Ten categories account for 76% of the potential ozone, while the remaining 38 categories account for 24%. Sales of Flat coatings add up to 1/3 of total architectural coating sales, but Flat coatings only represent 1/6 of the potential ozone.

Figure 2-2
Top 10 Categories for Maximum Potential Ozone

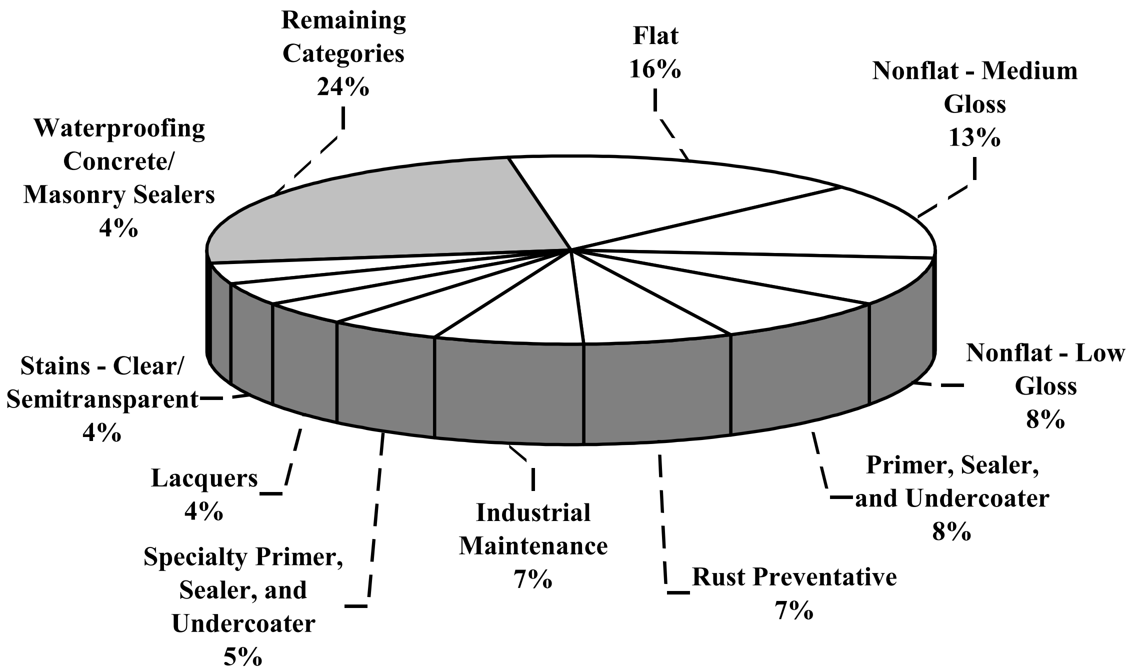
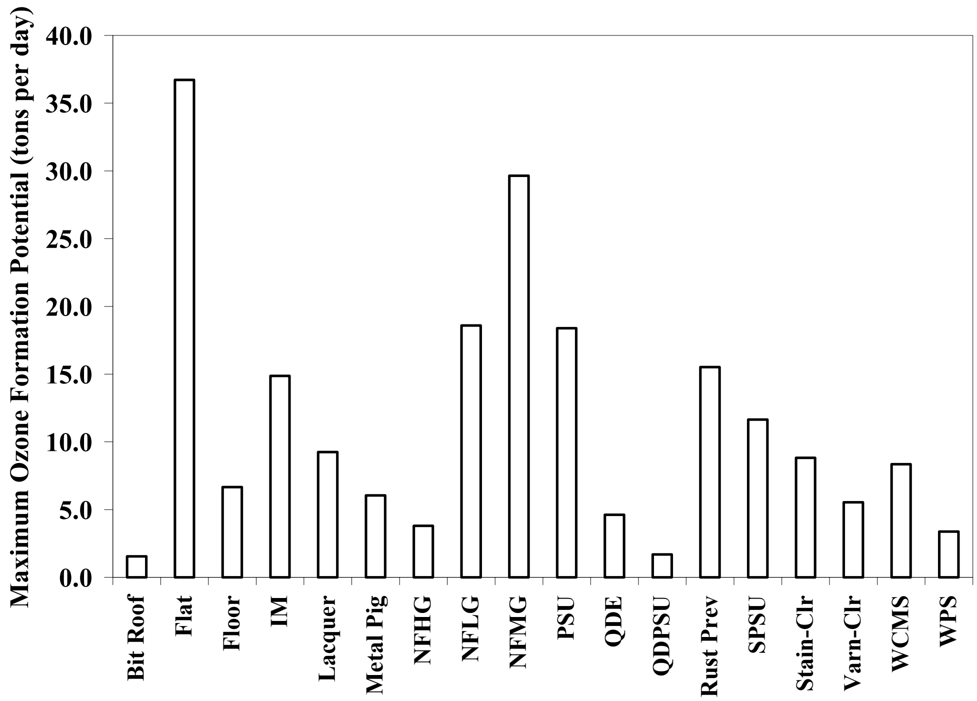


Figure 2-3 illustrates the “Maximum Ozone Formation Potential” for selected categories. Detailed data for all categories are provided in Table 2-2.

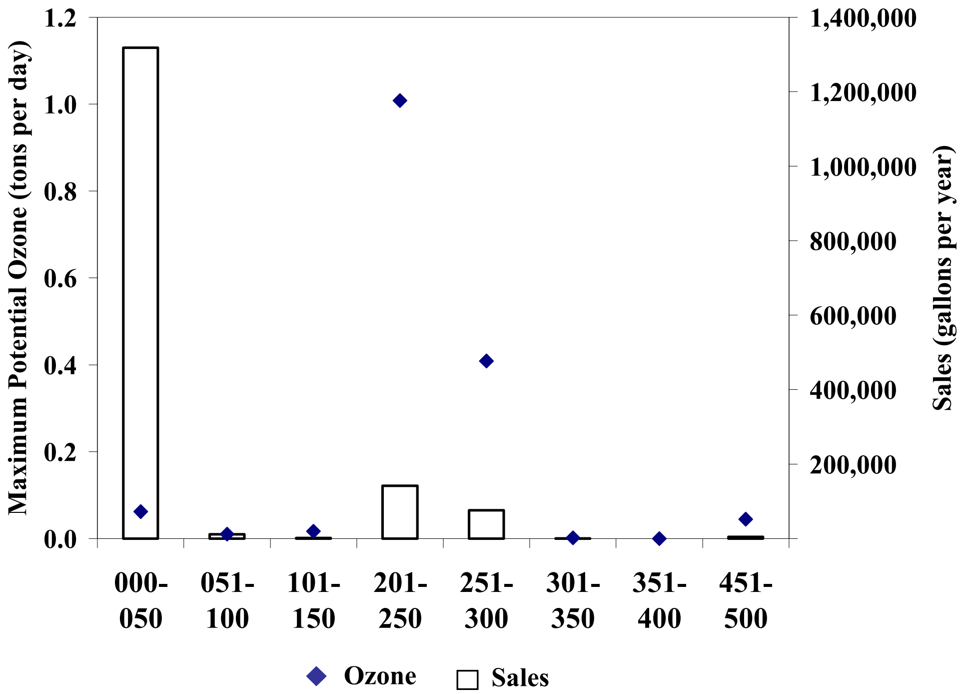
Figure 2-3
Maximum Ozone Formation Potential by Category



Notes:
1. [Maximum Ozone Formation Potential] = ∑ [Ingredient Emissions, tons/day]*[MIR, g Ozone/g Ingredient]
2. This figure includes data from small containers (1 quart or less).
3. This figure includes ozone generated from all volatile emissions, including VOCs and exempt compounds.

Figures 2-4 to 2-21 plot "Maximum Ozone Formation Potential" (tons/day) against "VOC Regulatory" values in 50-gram/liter increments. The figures also contain "Sales" (gallons/year) plotted against "VOC Regulatory". The figures include data from small containers and they represent ozone generated by emissions from all volatile compounds, including VOCs and exempt compounds. Figures are only included for selected categories. Detailed data for all categories are provided in Appendix B.

Figure 2-4
Bituminous Roof



This figure shows that the majority of the sales for this category had a low VOC content and these low-VOC products generated a relatively small amount of potential ozone. Products in the mid-range (200-300 g/l) generated most of the potential ozone, even though their sales were relatively small. This indicates that these mid-range products contained much more reactive solvents on a per-gallon basis as compared to the low-VOC products.

This figure is not typical of the ozone/sales figures in this chapter, as is shown on subsequent charts. In most cases, high amounts of ozone correspond to high sales volumes and low amounts of ozone correspond to low sales volumes. For those cases where the ozone diamond is much higher than the sales bar, that indicates products with relatively high reactivity per gallon. For those cases, where the ozone diamond is far below the top of the sales bar, that indicates products with relatively low reactivity per gallon.

Figure 2-5
Flat

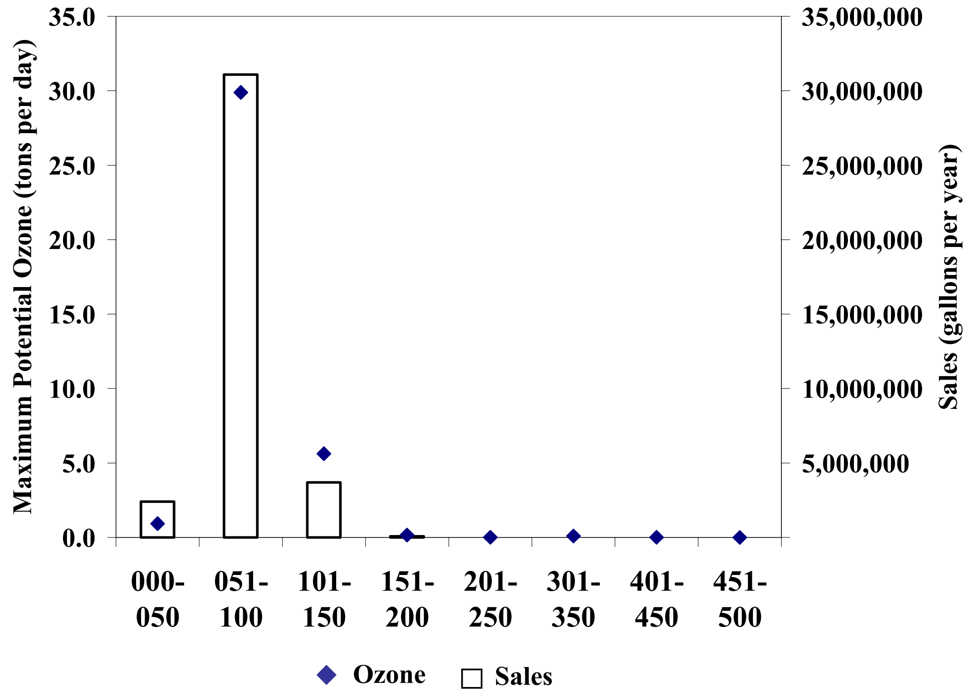


Figure 2-6
Floor

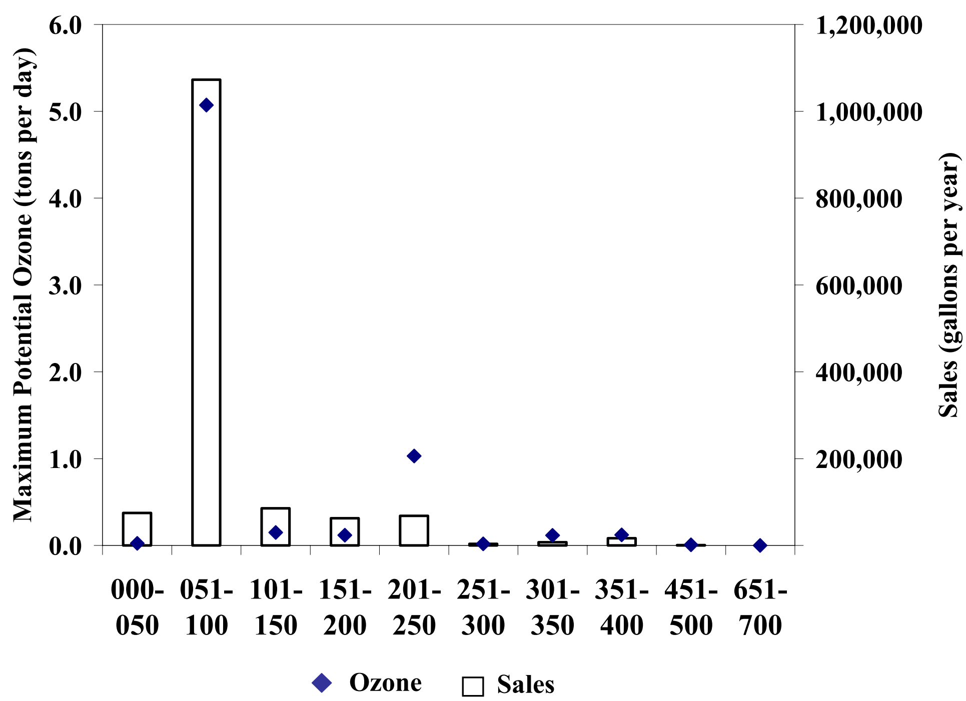


Figure 2-7
Industrial Maintenance

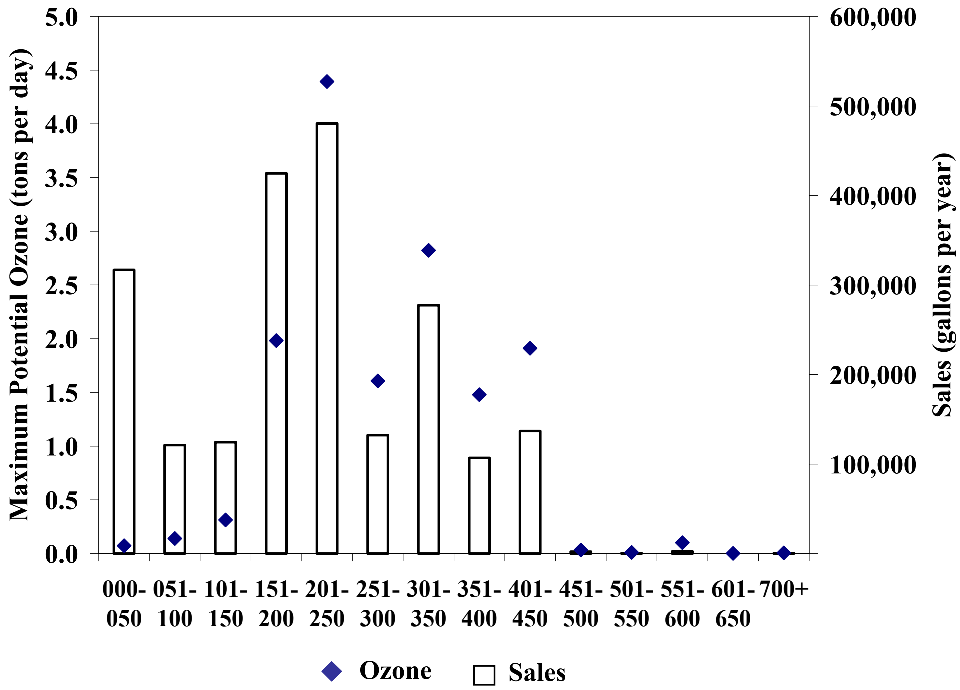


Figure 2-8
Lacquers

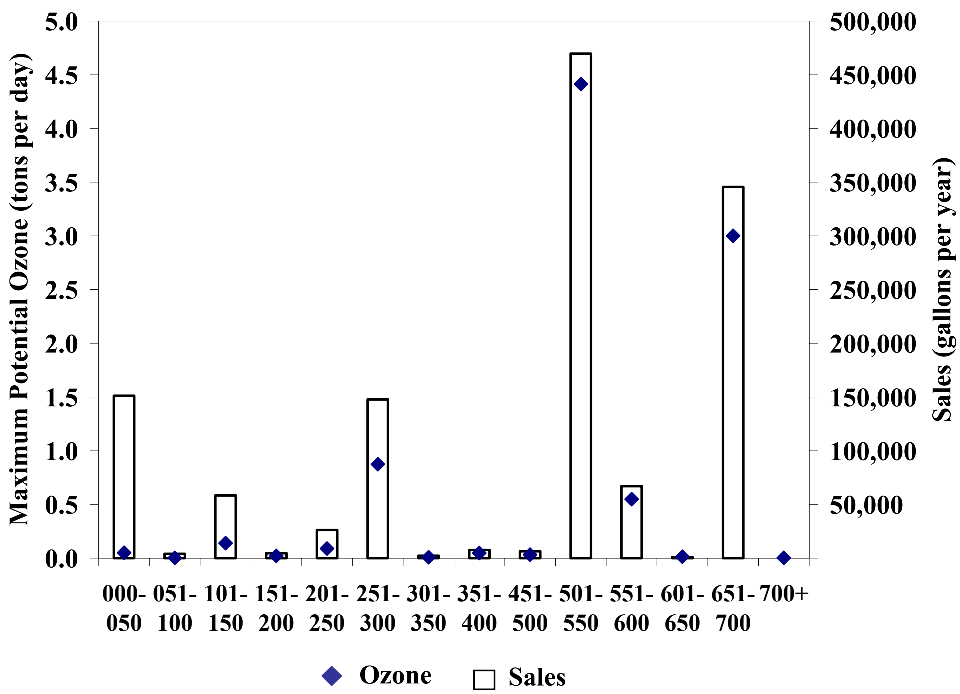


Figure 2-9
Metallic Pigmented

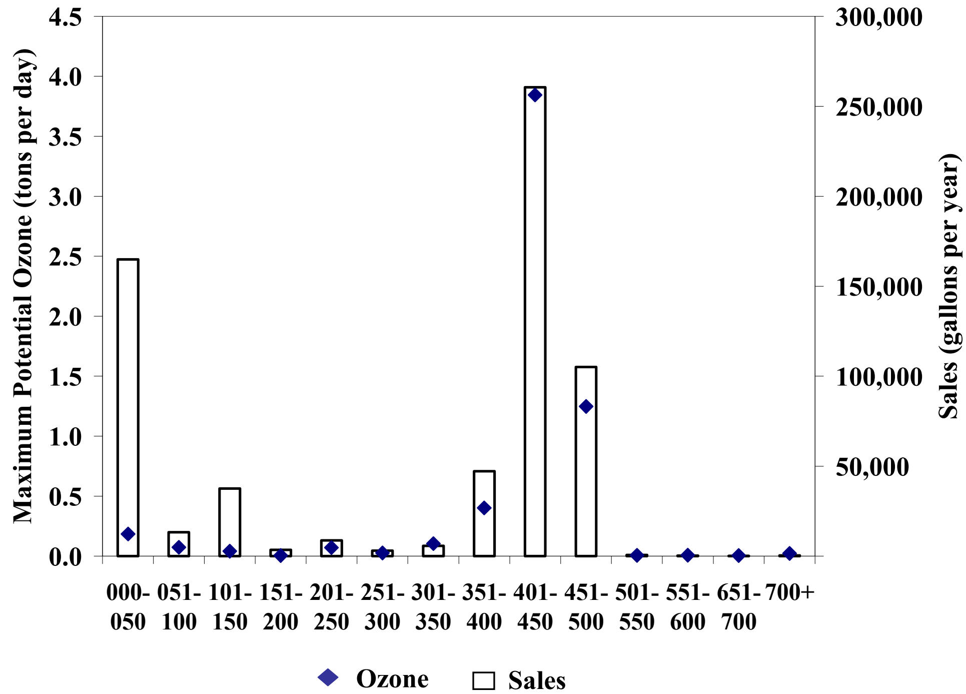


Figure 2-10
Nonflat – High Gloss

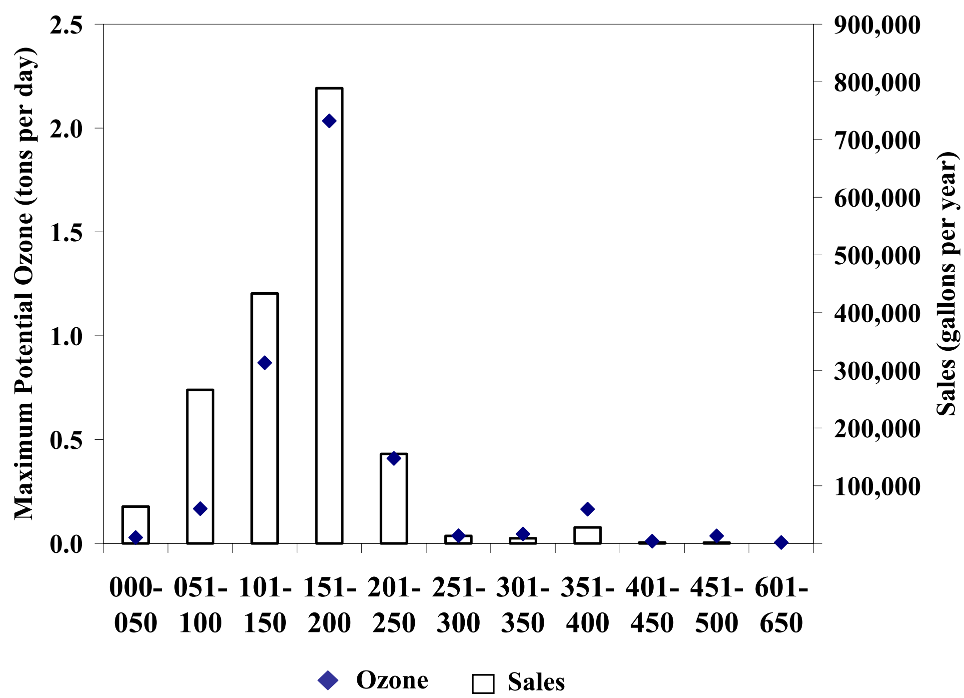


Figure 2-11
Nonflat – Low Gloss

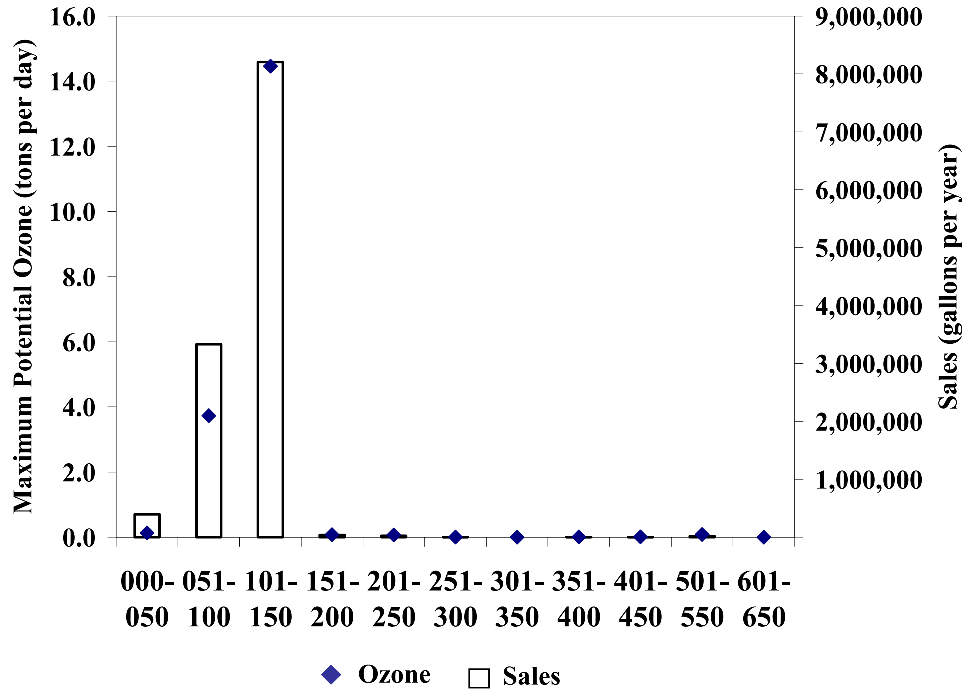


Figure 2-12
Nonflat – Medium Gloss

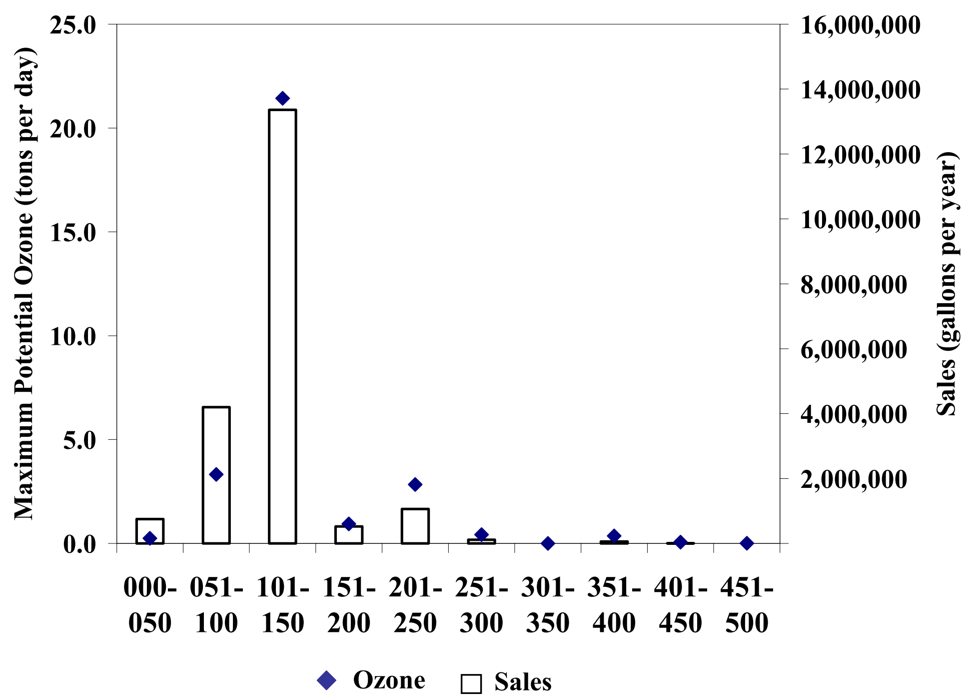


Figure 2-13
Primer, Sealer, Undercoater

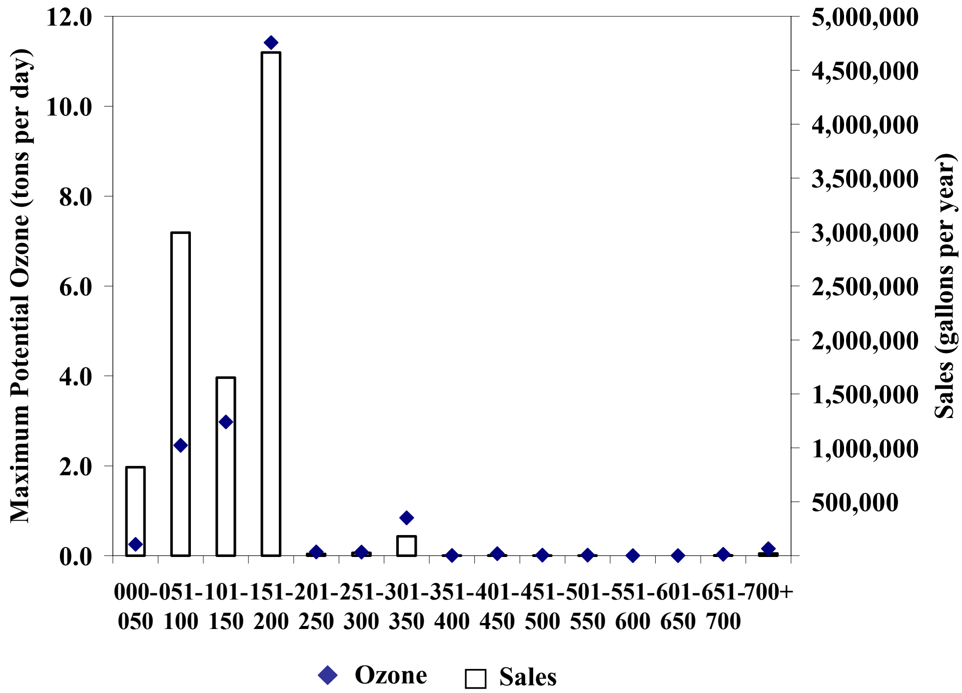


Figure 2-14
Quick Dry Enamel

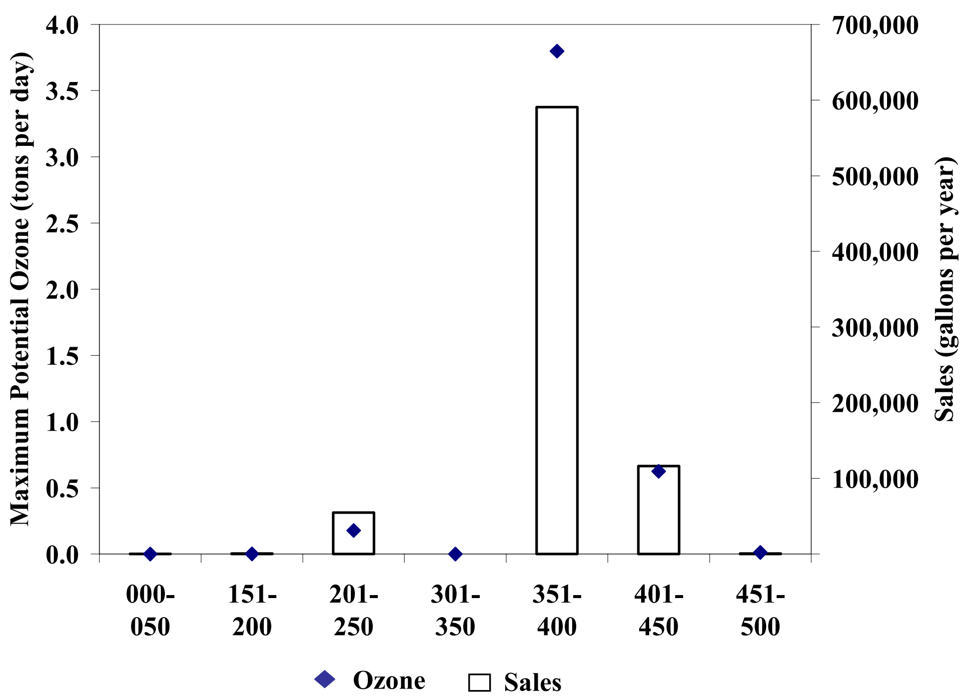


Figure 2-15
Quick Dry Primer, Sealer, Undercoater

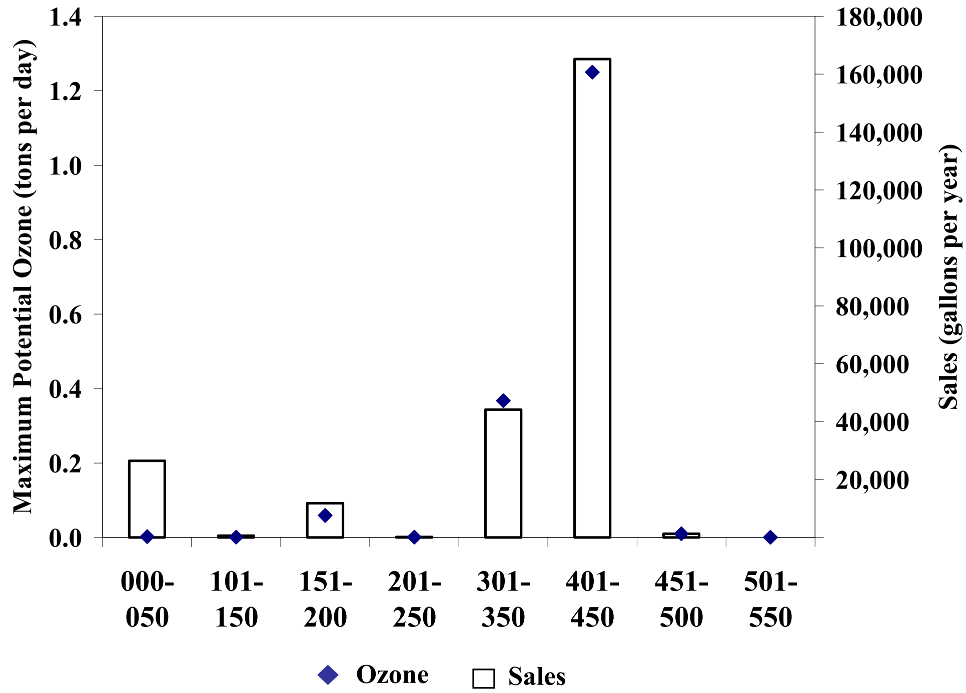


Figure 2-16
Rust Preventative

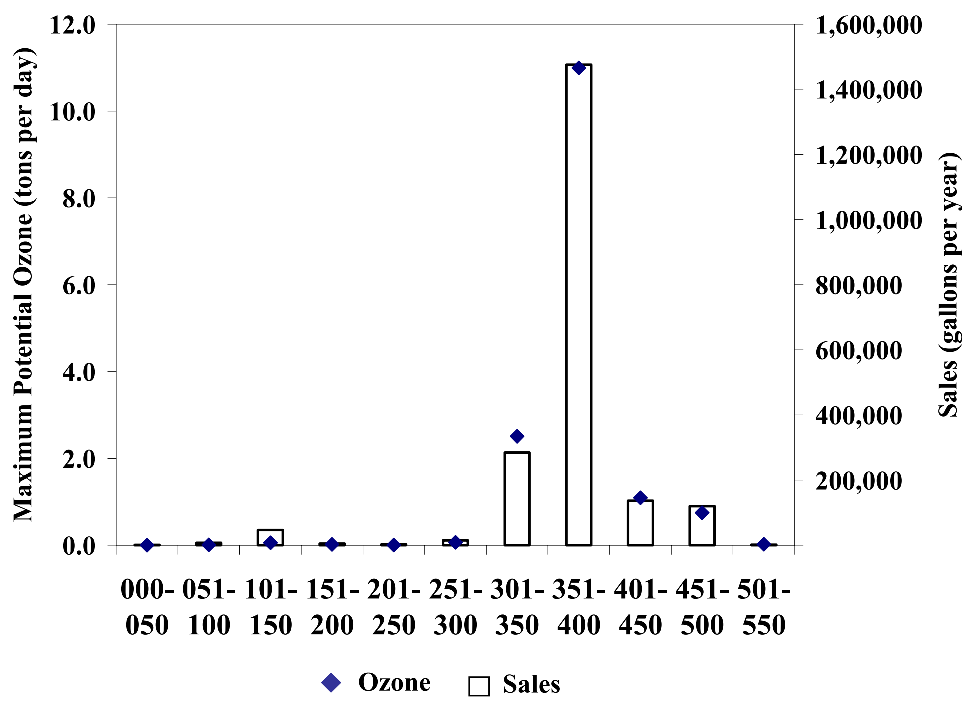


Figure 2-17
Specialty Primer, Sealer, Undercoater

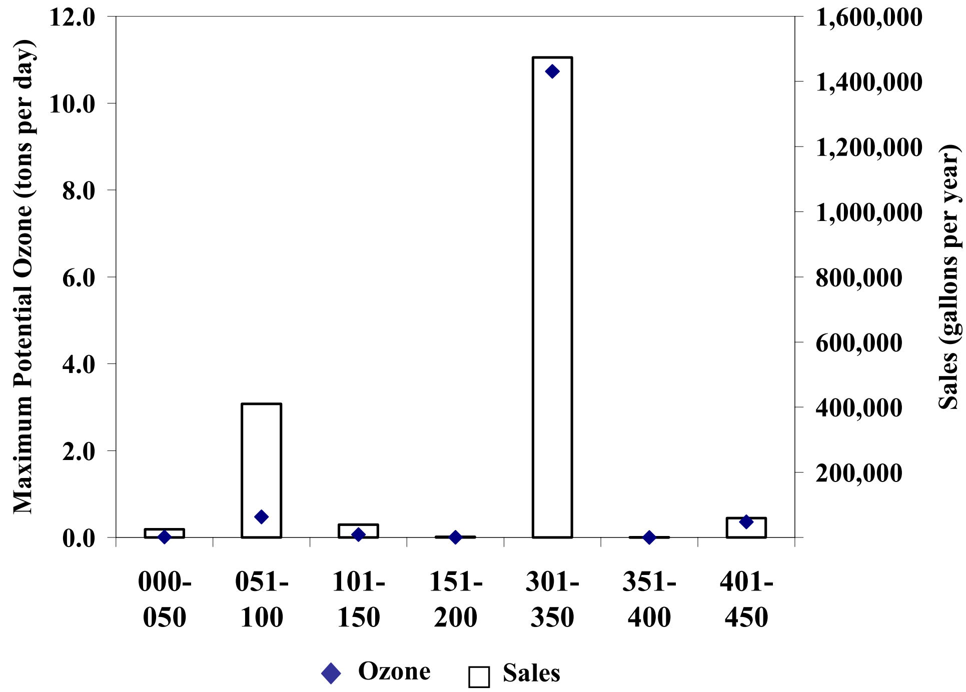


Figure 2-18
Stains – Clear/Semitransparent

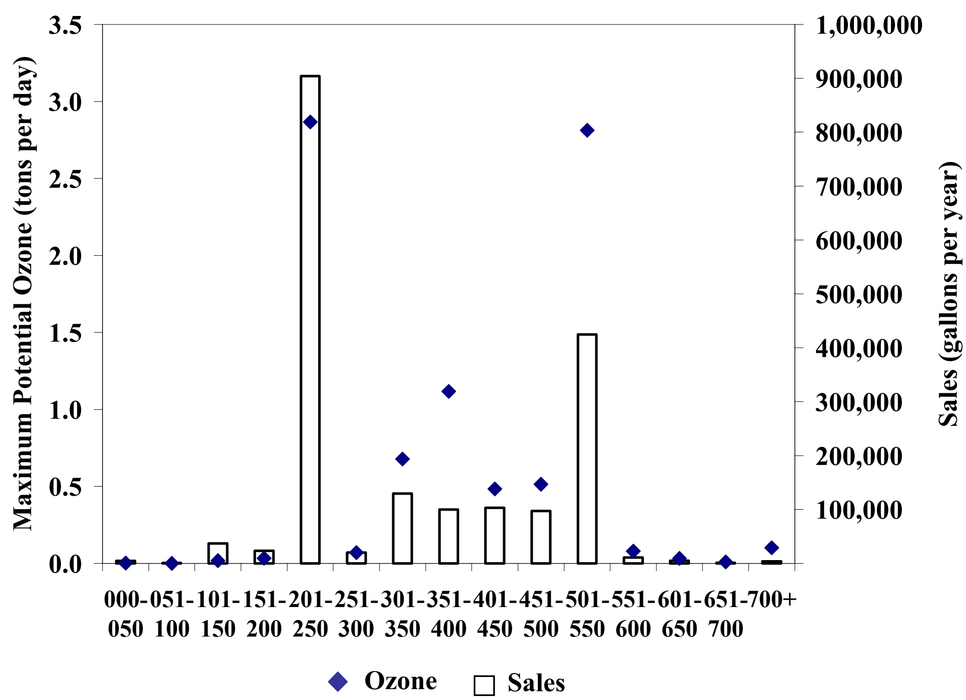


Figure 2-19
Varnishes - Clear

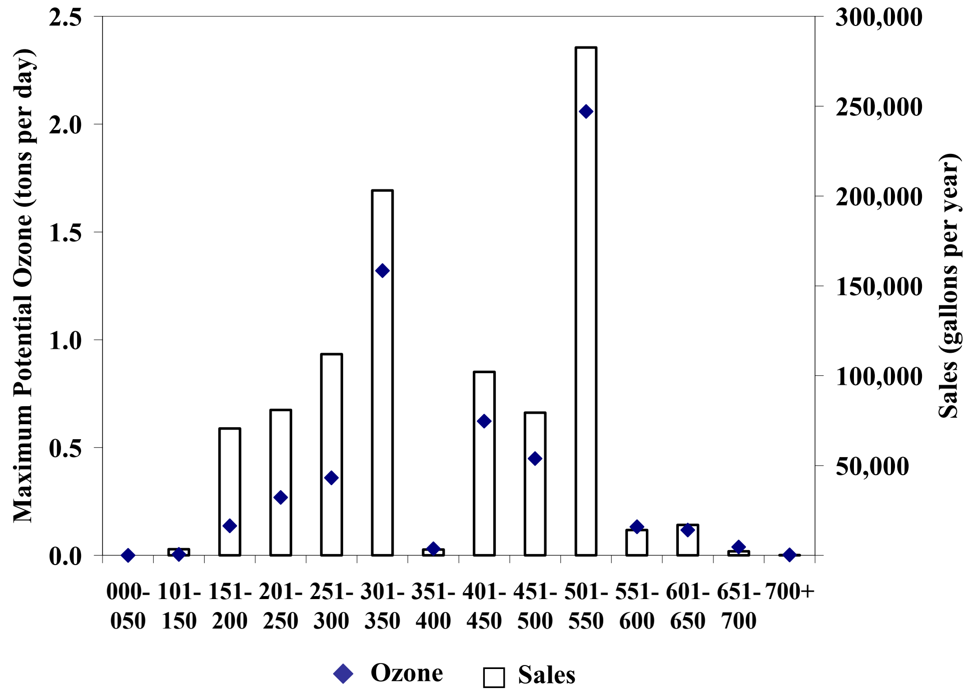


Figure 2-20
Waterproofing Concrete/Masonry Sealers

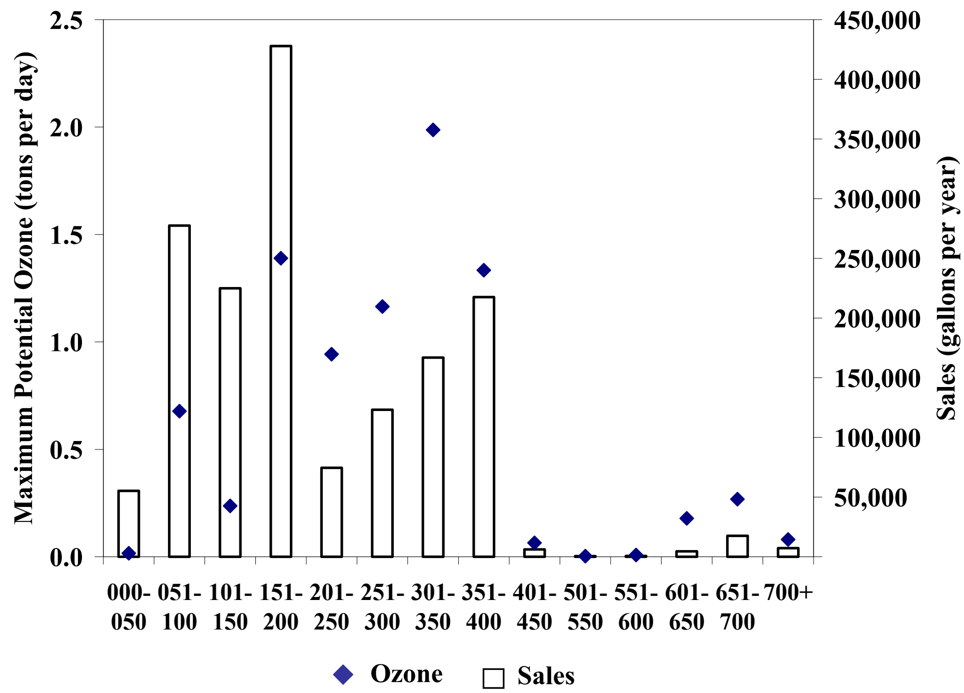
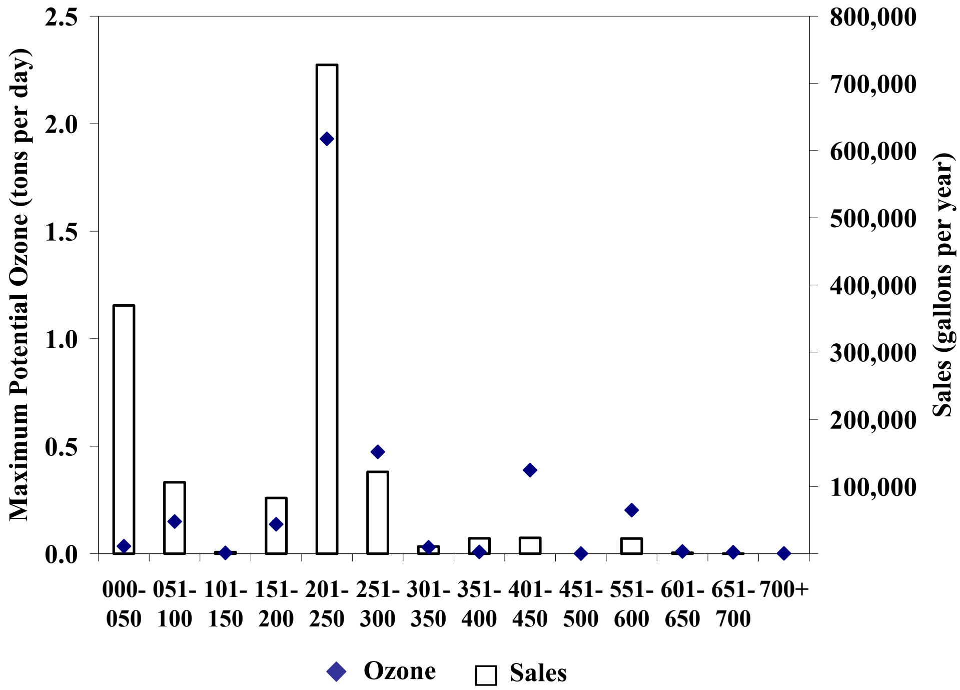


Figure 2-21
Waterproofing Sealers



Section 2.3 Possible Reactivity Formats

After determining the maximum ozone formation potential, it is necessary to normalize the values in a way that allows comparison between the different coating categories. In this section we will be considering the following possible approaches:

- Ozone Per Pound of Coating
- Ozone Per Gallon of Coating
- Ozone Per Pound of Solids
- Ozone Per Gallon of Solids

"Ozone Per Pound of Coating" is equivalent to the format that is used in ARB's Aerosol Coatings Regulation. For aerosol coatings, ARB has defined a "Product-Weighted MIR" (PWMIR) in units of grams ozone per gram product. The advantage of using a similar format would be consistency between aerosol coatings and architectural coatings reactivity-based regulations. In addition, U.S. EPA has already approved ARB's Aerosol Coatings Regulation. Therefore, using a similar approach would be helpful in obtaining U.S. EPA approval if districts adopted reactivity-based architectural coatings regulations. "Ozone Per Pound of Coating" was calculated as shown below:

[Ozone Per Pound of Coating] = [Total Ozone, lbs]/[Coating Mass, lbs]

[Coating Mass, lbs] = [Coating Sales, gallons]*[Coating Density, lb/gal]

These equations yield the same format as the Aerosol Coating Product-Weighted MIR which is calculated as follows:

$$[\text{PWMIR, g } O_3/\text{g product}] = [Wt\%]_1*[MIR]_1 + [Wt\%]_2*[MIR]_2 + \ldots + [Wt\%]_n*[MIR]_n$$

where

$[Wt\%]_i$ = the weight percent of each ingredient in a coating product (e.g., 0.25 for 25%)
$[MIR]_i$ = the MIR value of each ingredient in a coating product, g O_3/g TOG
n = the total number of ingredients in a coating product

An example is provided below, based on actual survey data that has been altered slightly to protect manufacturer confidentiality:

Coating Sales = 5,000 gals
Coating Density = 9 lbs/gal
Coating Mass = [5,000 gals]*[9 lbs/gal] = 45,000 lbs

Ingredient	**CAS #**	**Wt %**	**Ingr. Mass (lbs ingred)**	**MIR (gram O_3/ gram ingred)**	**Maximum Potential Ozone (lbs O3)**
1,2-Propanediol	57-55-6	4%	1,800	2.74	4,932
2,2,4-Trimethyl-1,3-Pentanediol Monoisobutyrate	25265-77-4	2%	900	0.88	792
2-(2-Butoxyethoxy)-Ethanol	112-34-5	4%	1,800	2.87	5,166
2-(2-Methoxyethoxy)-Ethanol	111-77-3	3%	1,350	2.88	3,888
Water	7732-18-5	54%	24,300	0	0
Solids		33%	14,850	0	0
	TOTAL =	**100%**	**45,000 lbs**		**14,778 lbs O3**
Lbs Ozone Per Lb Coating = [14,778]/[45,000] = **0.33**					

Ingredient	**CAS #**	**Wt %**	**MIR (g O_3/g TOG)**	**[Wt%]*[MIR]**
1,2-Propanediol	57-55-6	4%	2.74	0.110
2,2,4-Trimethyl-1,3-Pentanediol Monoisobutyrate	25265-77-4	2%	0.88	0.018
2-(2-Butoxyethoxy)-Ethanol	112-34-5	4%	2.87	0.115
2-(2-Methoxyethoxy)-Ethanol	111-77-3	3%	2.88	0.086
Water	7732-18-5	54%	0	0
Solids		33%	0	0
	TOTAL =	**100%**		**0.33**
Product-Weighted MIR = **0.33** grams ozone/gram product				

"Ozone Per Gallon of Coating" is similar to the format of "VOC Actual" which expresses "VOC Emissions Per Gallon of Coating". It's also similar to the format of emission factors for coatings which can be used to develop emission inventories. "Ozone Per Gallon of Coating" was calculated as shown below:

[Ozone Per Gallon of Coating] = [Total Ozone, lbs]/[Coating Sales, gallons]

"Ozone Per Pound of Solids" is similar to the format that U.S. EPA uses for wood coatings rules. The National Emission Standards for Hazardous Air Pollutants (NESHAPs) for Wood Furniture Manufacturing includes emission limits in units of "lb VHAP/lb solids" (i.e., pounds of volatile hazardous air pollutant per pound of solids). According to U.S. EPA, "…The traditional method for coatings of g/L less water is not appropriate for HAP's because there is not always a direct relationship between the HAP content of a coating and the solids content of a coating..." (U.S. EPA, 1995) For the sake of consistency, U.S. EPA used similar units for their Control Techniques Guidelines (CTG) for wood furniture manufacturing operations which has emission limits in units of "lb VOC/lb solids" (i.e., pounds of volatile organic compounds per pound of solids) (U.S. EPA, 1996.) U.S. EPA also considered units of "lb VOC/gallon solids", but they were concerned that there was no U.S. EPA test method available to accurately measure the volume of solids.

[Ozone Per Pound of Solids] = [Total Ozone, lbs]/[Solids Mass, lbs]

[Solids Mass, lbs] = [Coating Sales, gallons]*[Coating Density, lb/gal]*[Weight % Solids]

"Ozone Per Gallon of Solids" is a format that some consider to be the most appropriate format, because it is based on the volume of coating film that actually remains on the substrate after all of the volatiles have evaporated. In addition, volume of solids corresponds to coverage and dry film thickness, which are critical parameters for many coatings.

[Ozone Per Gallon of Solids] = [Total Ozone, lbs]/[Solids Volume, gallons]

[Solids Volume, gals] = [Coating Sales, gallons]*[Volume % Solids]

Table 2-3 summarizes the various formats for each coating category. Detailed data are contained in Appendix B for the following formats: Ozone Per Pound of Coating; Ozone Per Gallon of Coating; and Ozone Per Gallon of Solids.

Table 2-3: ***Possible Ozone Reactivity Formats***

	Lb Ozone Per Lb Coating			*Lb Ozone Per Gal Coating*			*Lb Ozone Per Lb Solids*			*Lb Ozone Per Gal Solids*		
Coating Category	**SB**	**WB**	**All**	**SB**	**WB**	**All**	**SB**	**WB**	**All**	**SB**	**WB**	**All**
Bituminous Roof	0.6	0.0	0.1	4.8	0.0	0.7	0.7	0.0	0.2	6.9	0.1	1.4
Bituminous Roof Primer	0.8	0.2	0.7	5.9	1.7	5.4	1.3	0.5	1.2	10.0	4.7	9.6
Bond Breakers	1.5	0.4	0.4	10.8	2.9	3.0	9.9	2.2	2.2	98.0	16.7	16.9
Clear Brushing Lacquer	1.5	NA	1.5	11.2	NA	11.2	5.7	NA	5.7	59.8	NA	59.8
Concrete Curing Compounds	1.5	0.1	0.2	12.1	0.9	1.4	3.6	0.6	0.9	48.8	5.3	8.4
Driveway Sealer	0.9	0.0	0.0	6.7	0.0	0.0	1.8	0.0	0.0	13.4	0.0	0.1
Dry Fog	0.5	0.1	0.3	5.9	0.8	3.3	0.7	0.1	0.4	12.9	2.1	7.9
Faux Finishing	0.5	0.2	0.2	4.7	2.3	2.3	0.8	0.6	0.6	10.5	7.9	8.0
Fire Resistive	0.6	0.0	0.3	6.1	0.2	2.6	0.7	0.0	0.4	8.0	0.4	4.4
Fire Retardant - Clear	2.3	NA	2.3	19.6	NA	19.6	4.6	NA	4.6	50.6	NA	50.6
Fire Retardant - Opaque	0.3	0.0	0.3	3.7	0.1	3.3	0.4	0.0	0.4	6.6	0.4	6.2
Flat	1.7	0.1	0.1	18.1	0.7	0.7	2.3	0.1	0.1	29.7	2.0	2.0
Floor	0.8	0.3	0.4	7.4	3.2	3.6	1.0	0.7	0.7	9.4	9.1	9.1
Form Release Compounds	0.4	0.1	0.4	3.3	0.5	3.0	0.6	0.4	0.6	4.7	3.2	4.6
Graphic Arts	0.4	0.3	0.4	4.3	2.4	3.9	0.5	0.5	0.5	8.6	6.1	8.2
High Temperature	0.8	NA	0.8	8.7	NA	8.7	1.4	NA	1.4	20.2	NA	20.2
Industrial Maintenance	0.6	0.2	0.5	7.0	1.8	5.2	0.8	0.4	0.7	9.7	4.5	8.6
Lacquers	0.9	0.1	0.6	6.6	1.5	5.2	2.9	0.3	1.8	30.7	4.7	21.2
Low Solids	NA	0.1	0.1	NA	1.2	1.2	NA	1.5	1.5	NA	13.6	13.6
Magnesite Cement	2.3	NA	2.3	20.1	NA	20.1	4.7	NA	4.7	60.3	NA	60.3
Mastic Texture	0.2	0.1	0.1	1.6	0.9	1.0	0.3	0.1	0.1	3.1	1.8	2.0
Metallic Pigmented	0.5	0.1	0.4	8.2	1.4	6.8	0.6	0.3	0.6	13.7	3.9	12.4
Multi-Color	0.7	0.0	0.0	5.7	0.3	0.4	2.6	0.1	0.1	34.6	1.4	1.8
Nonflat - High Gloss	0.5	0.1	0.2	4.8	1.5	1.6	0.8	0.3	0.3	9.3	4.3	4.5
Nonflat - Low Gloss	0.4	0.1	0.1	4.7	1.1	1.1	0.6	0.2	0.2	9.9	3.2	3.2
Nonflat - Medium Gloss	0.4	0.1	0.1	4.3	1.1	1.1	0.6	0.2	0.2	8.0	3.2	3.2

Table 2-3: ***Possible Ozone Reactivity Formats***

	Lb Ozone Per Lb Coating			*Lb Ozone Per Gal Coating*			*Lb Ozone Per Lb Solids*			*Lb Ozone Per Gal Solids*		
Coating Category	**SB**	**WB**	**All**	**SB**	**WB**	**All**	**SB**	**WB**	**All**	**SB**	**WB**	**All**
Other	2.0	0.0	0.1	18.9	0.1	0.6	3.8	0.0	0.2	54.8	0.5	3.1
Pre-Treatment Wash Primer	1.8	0.1	0.4	13.4	1.0	3.4	10.5	0.4	1.3	170.4	4.7	17.5
Primer, Sealer, and Undercoater	0.4	0.1	0.1	4.0	1.2	1.3	0.5	0.2	0.2	7.8	3.7	3.9
Quick Dry Enamel	0.5	0.2	0.5	4.6	2.4	4.4	0.7	0.5	0.7	9.1	7.3	9.0
Quick Dry Primer, Sealer, and Undercoater	0.5	0.0	0.5	5.6	0.1	4.9	0.8	0.0	0.7	12.9	0.4	11.6
Roof	0.8	0.0	0.1	7.8	0.4	0.6	1.0	0.1	0.1	11.2	0.9	1.4
Rust Preventative	0.5	0.2	0.5	5.6	1.6	5.4	0.8	0.4	0.8	10.7	4.9	10.6
Sanding Sealers	0.8	0.1	0.6	6.0	1.2	4.6	2.0	0.5	1.6	18.0	4.2	14.6
Shellacs - Clear	1.0	NA	1.0	7.7	NA	7.7	3.7	NA	3.7	36.6	NA	36.6
Shellacs - Opaque	0.7	NA	0.7	6.4	NA	6.4	1.2	NA	1.2	20.4	NA	20.4
Specialty Primer, Sealer, and Undercoater	0.4	0.1	0.4	5.3	0.9	4.2	0.6	0.1	0.5	9.6	2.1	8.2
Stains - Clear/Semitransparent	0.5	0.2	0.5	4.1	1.3	3.5	0.9	0.7	0.9	7.8	6.9	7.7
Stains - Opaque	0.5	0.1	0.1	5.4	1.0	1.1	0.7	0.2	0.2	9.2	2.7	3.0
Swimming Pool	1.0	0.3	0.8	12.0	3.6	8.9	1.2	0.6	1.1	17.6	9.3	15.5
Swimming Pool Repair and Maintenance	3.5	NA	3.5	36.4	NA	36.4	6.6	NA	6.6	105.3	NA	105.3
Traffic Marking	0.4	0.1	0.1	5.2	0.7	1.4	0.5	0.1	0.1	9.5	1.3	2.5
Varnishes - Clear	0.7	0.3	0.5	4.9	2.2	4.2	1.4	0.9	1.3	11.7	7.9	10.9
Varnishes - Semitransparent	0.5	0.2	0.4	3.6	1.5	3.4	0.9	0.4	0.9	8.3	5.0	8.1
Waterproofing Concrete/Masonry Sealers	0.6	0.1	0.4	5.6	1.4	3.9	0.8	0.3	0.6	9.0	3.8	7.6
Waterproofing Sealers	0.6	0.1	0.2	4.7	1.2	1.7	1.0	0.5	0.6	9.7	4.9	6.0

Table 2-3: ***Possible Ozone Reactivity Formats***

	Lb Ozone Per Lb Coating			*Lb Ozone Per Gal Coating*			*Lb Ozone Per Lb Solids*			*Lb Ozone Per Gal Solids*		
Coating Category	**SB**	**WB**	**All**	**SB**	**WB**	**All**	**SB**	**WB**	**All**	**SB**	**WB**	**All**
Wood Preservatives	0.6	0.1	0.6	4.2	1.1	4.0	0.9	1.2	0.9	7.0	10.1	7.1

Notes:

1. "Lb Ozone": Maximum Ozone Formation Potential under MIR conditions.
2. "Lb Ozone Per Lb Coating": Total pounds of ozone for a category divided by the total pounds of coating for the category.
3. "Lb Ozone Per Gal Coating": Total pounds of ozone for a category divided by the total gallons of coating for the category.
4. "Lb Ozone Per Lb Solids": Total pounds of ozone for a category divided by the total pounds of solids for the category.
5. "Lb Ozone Per Gal Solids": Total pounds of ozone for a category divided by the total gallons of solids for the category.
6. "NA": Not Applicable because no coating sales were reported or inadequate data were reported.
7. This table includes data from small containers (1 quart or less).
8. This table includes ozone generated from all volatile emissions, including VOCs and exempt compounds.

Section 2.4 Sales-Weighted Average MIR Values

Sales-weighted average MIR values (SWAMIRs) provide another way to characterize the overall reactivity of a given category. In most cases, SWAMIRs are similar to the category-wide ozone values shown in Table 2-3 that don't include any sales-weighting. However, it is important to note that SWAMIRs can sometimes be quite different than the values in Table 2-3, because they are based on inherently different calculations. Sales-weighting assigns greater importance to products that have higher sales volumes, while the values in Table 2-3 are based on total ingredients without consideration of which ingredients are in high volume products. Therefore, if a category has a particularly dominant product, the SWAMIR for that category will be more reflective of the dominant product.

To determine SWAMIRs, we used the following equation:

$$\text{SWAMIR} = \frac{[\text{Sales}]_1 * [\text{Lb O3/Lb Coating}]_1 + [\text{Sales}]_2 * [\text{ Lb O3/Lb Coating}]_2 + \ldots + [\text{Sales}]_n * [\text{ Lb O3/Lb Coating}]_n}{[\text{Sales}]_1 + [\text{Sales}]_2 + \ldots + [\text{Sales}]_n}$$

where

$[\text{Sales, gals}]_i$ = the sales of product "i", gallons
$[\text{Lb O3/Lb Coating}]_i$ = the [Maximum Ozone Formation Potential, lbs]/[Mass of Coating, lbs] for each product
n = the total number of coating products

An example is provided below:

Product	[Lb O3/Lb Coating]	Sales (gals)	[Lb O3/Lb Coating]*[Sales]
#1	0.75	1,000	750
#2	1.16	12,000	13,920
#3	0.98	3,500	3,430
#4	0.35	500	175
	TOTALS:	**17,000**	**18,275**
Sales-Weighted Avg. MIR = (18,275)/(17,000) = **1.08** lbs ozone/lb coating			

SWAMIRs were calculated for all of the coating categories based on the 2005 survey data. The survey collected sales data for more than 11,000 products and it also gathered data on the chemical ingredients contained in each product. However, there were approximately 80 products for which no ingredient data were submitted. These 80 products only represent 0.2 percent of the total sales volume. Since ingredient data are required to identify MIRs, we did not include the products with missing ingredient data when calculating sales-weighted average MIR values.

SWAMIRs were not calculated for the units of [Lb Ozone/Gal Coating], because the individual sales volumes cancel out in the sales-weighted average equation, as shown below:

$$\text{SWAMIR} = \frac{[\cancel{\text{Sales}}]_1*[\text{Lb O3}/\cancel{\text{Sales}}]_1 + [\cancel{\text{Sales}}]_2*[\text{ Lb O3}/\cancel{\text{Sales}}]_2 +\ldots+[\cancel{\text{Sales}}]_n*[\text{ Lb O3}/\cancel{\text{Sales}}]_n}{[\text{Sales}]_1 + [\text{Sales}]_2 +\ldots+[\text{Sales}]_n}$$

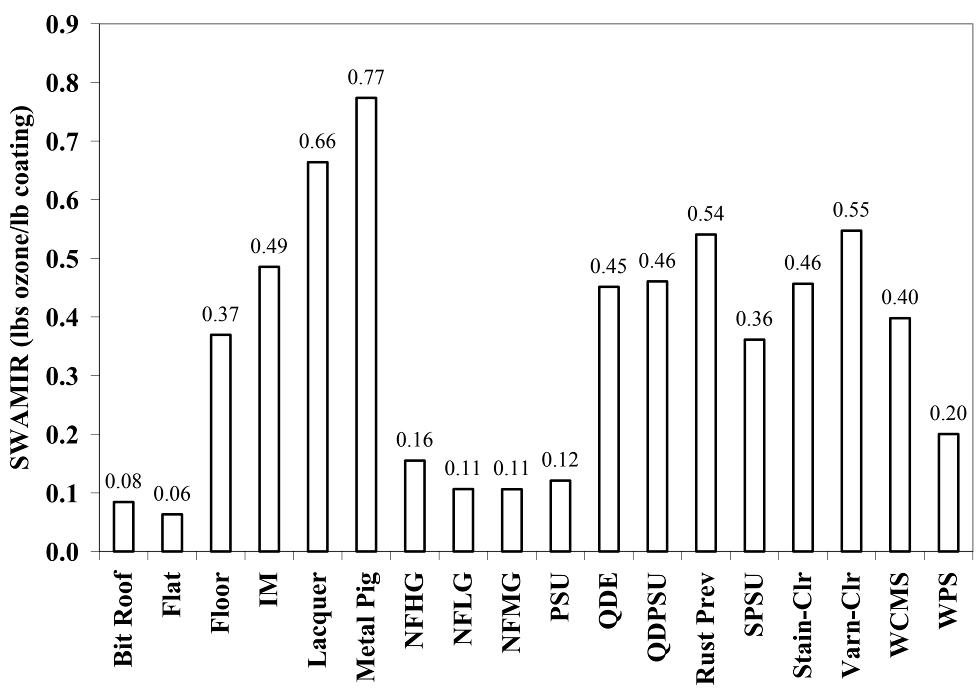
where

$[\text{Sales, gals}]_i$ = the sales of product “i”, gallons
$[\text{Lb O3/Sales}]_i$ = the [Maximum Ozone Formation Potential, lbs]/[Sales, gals] for each product
n = the total number of coating products

Since sales-weighting is not possible for the units of [Lb Ozone/Gal Coating], we’ve provided the total ozone over the total gallons in Table 2-3.

Figure 2-22 contains SWAMIRs for selected coating categories. Data are provided in units of [Lb Ozone/Lb Coating], which corresponds to the approach that ARB used in the reactivity-based Aerosol Coatings Regulation.

Figure 2-22
Sales-Weighted Average MIR – [Lb Ozone/Lb Coating]



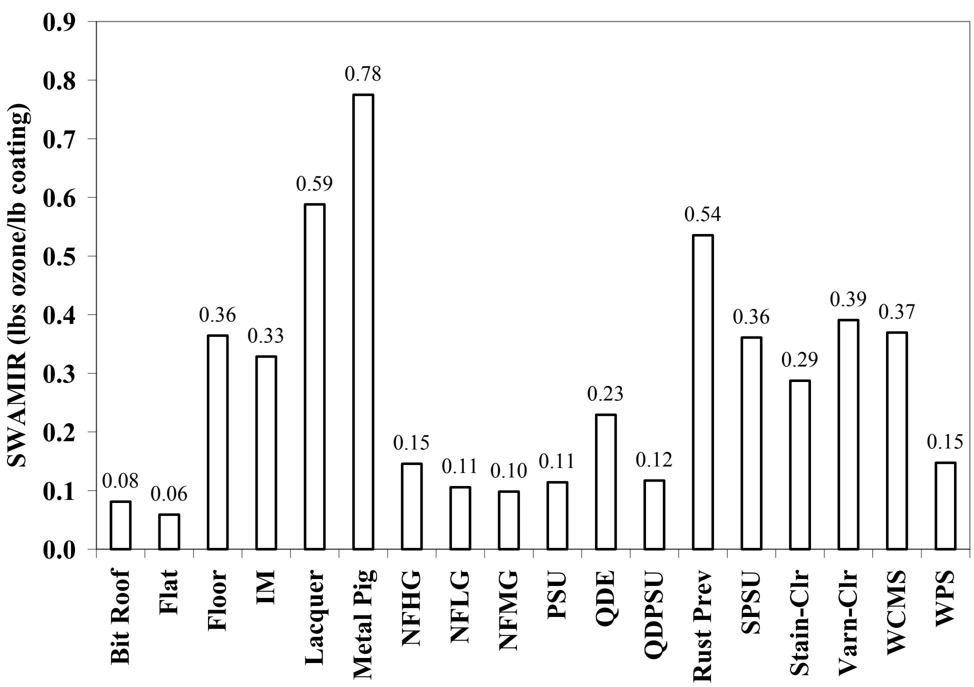
Notes:
1. [Lb Ozone]/[Lb Coating] = [Maximum Ozone Formation Potential]/[Total Coating Mass]
2. [Maximum Ozone Formation Potential] = ∑ [Ingredient Emissions, lbs]*[MIR, g Ozone/g Ingredient]
3. [Total Coating Mass] = ∑ [Coating Sales Volume, gals]*[Coating Density, lb/gal]
4. This figure includes data from small containers (1 quart or less).
5. This figure includes ozone generated from all volatile emissions, including VOCs and exempt compounds.

Detailed SWAMIR data for all coating categories are contained in Appendix B, including a breakdown for solventborne and waterborne formulations. Appendix B also contains

SWAMIRs for compliant and non-compliant coatings, based on the VOC limits contained in ARB's 2000 Architectural Coatings SCM and the SCAQMD VOC limits that will take effect in or before 2008.

Figure 2-23 contains data similar to Figure 2-22, but it provides SWAMIRs only for those reported coatings that complied with the VOC limits in ARB's 2000 Suggested Control Measure. In addition, Figure 2-23 does not include sales of small containers (one quart or less), because they are exempt from the SCM VOC limits. When comparing Figure 2-22 (all coatings) to Figure 2-23 (compliant coatings only), the SWAMIRs are similar for most of the categories. However, the SWAMIRs on Figure 2-23 are significantly lower for compliant coatings in the following categories: Industrial Maintenance; Quick Dry Enamel; Quick Dry Primer, Sealer, Undercoater; Stains – Clear/Semitransparent; and Varnishes - Clear.

Figure 2-23
Sales-Weighted Average MIR – [Lb Ozone/Lb Coating]
(Only Includes Compliant Coatings in Large Containers)



Notes:
1. [Lb Ozone]/[Lb Coating] = [Maximum Ozone Formation Potential]/[Total Coating Mass]
2. [Maximum Ozone Formation Potential] = ∑ [Ingredient Emissions, lbs]*[MIR, g Ozone/g Ingredient]
3. [Total Coating Mass] = ∑ [Coating Sales Volume, gals]*[Coating Density, lb/gal]
4. This figure only includes data for coatings that comply with the VOC limits in the 2000 SCM.
5. This figure does not include data from small containers (1 quart or less).
6. This figure includes ozone generated from all volatile emissions, including VOCs and exempt compounds.

Figures 2-24 to 2-41 contain charts of the SWAMIRs for selected categories in 50-gram/liter (g/l) ranges for VOC Regulatory. For each of the selected categories, two SWAMIR formats are provided: [Pounds Ozone per Pound Coating] and [Pounds Ozone per Gallon Solids]. Appendix B contains similar SWAMIR data for all categories. Appendix B also contains [Pounds Ozone per Gallon Coating] for all categories in 50-g/l ranges.

Figure 2-24
Bituminous Roof (lb O^3/lb coating)

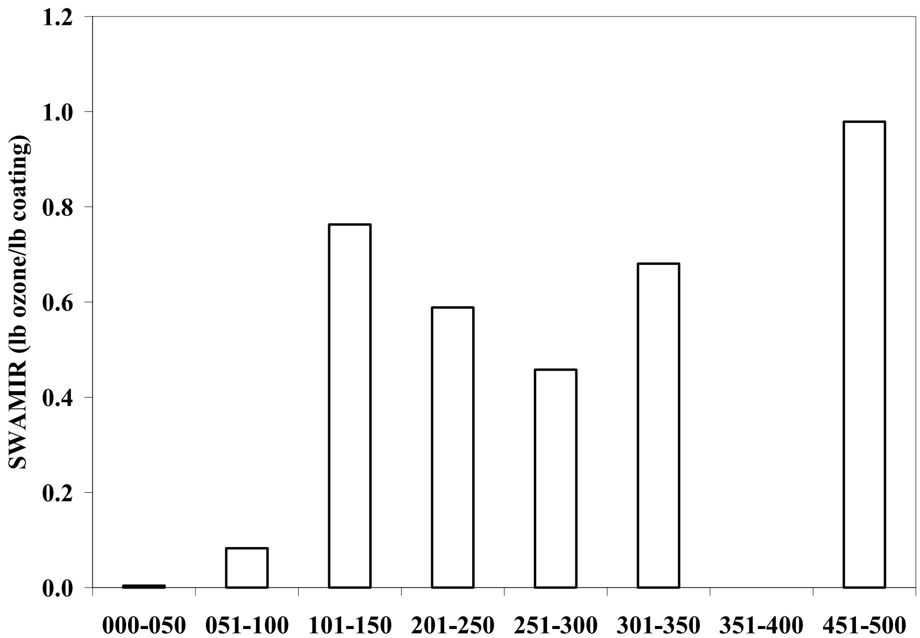


Figure 2-25
Bituminous Roof (lb O^3/gallon solids)

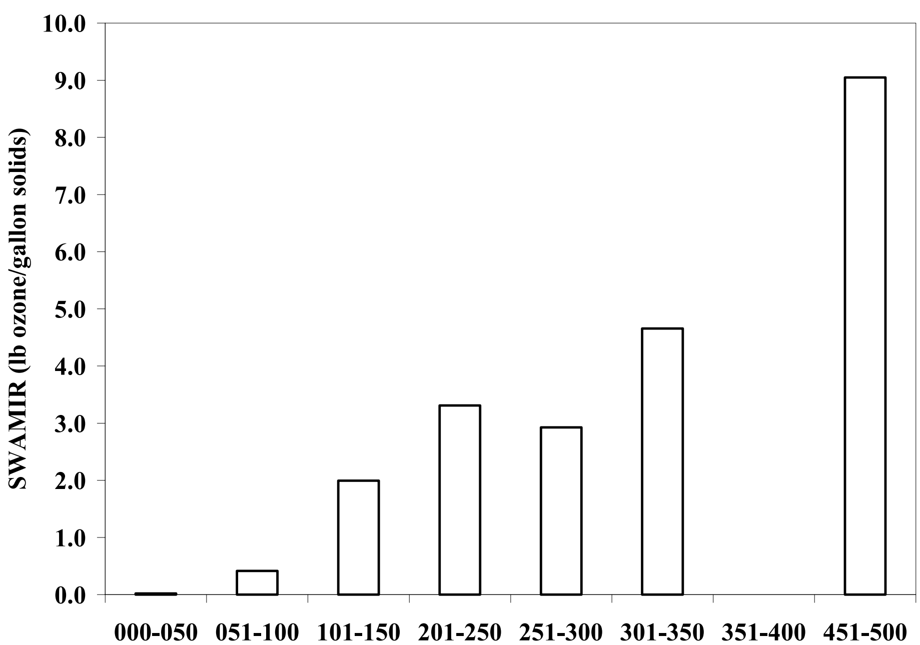


Figure 2-26
Flat (lb O^3/lb coating)

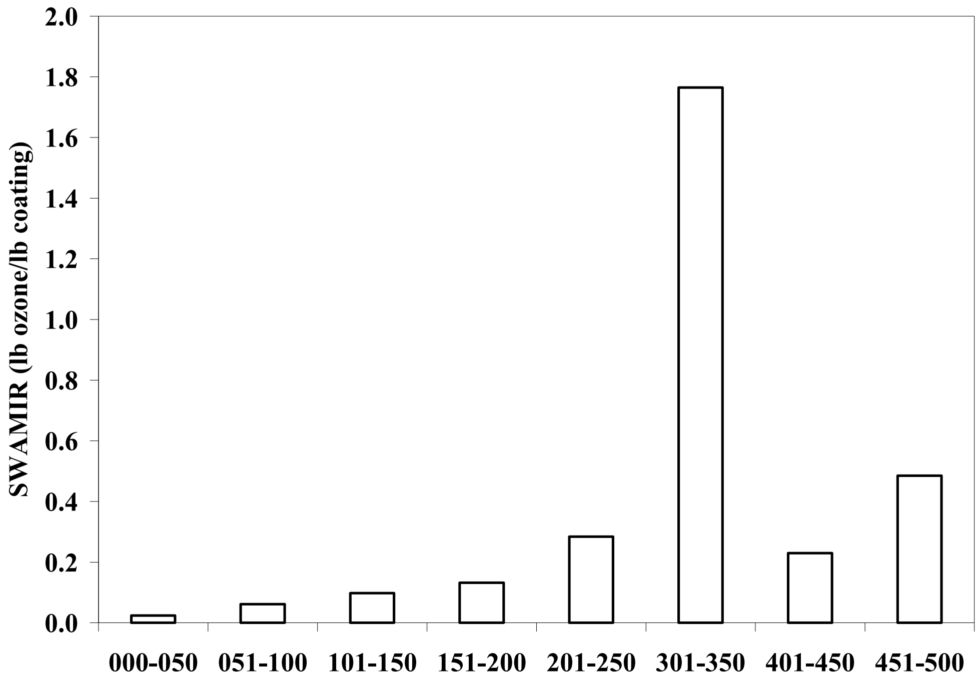


Figure 2-27
Flat (lb O^3/gallon solids)

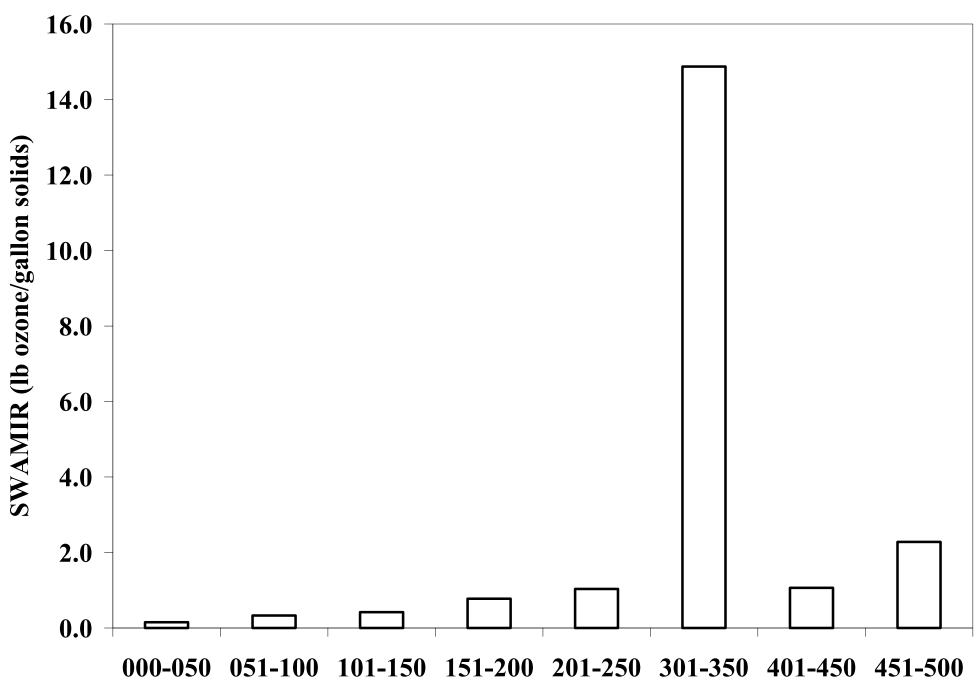


Figure 2-28
Floor (lb O3/lb coating)

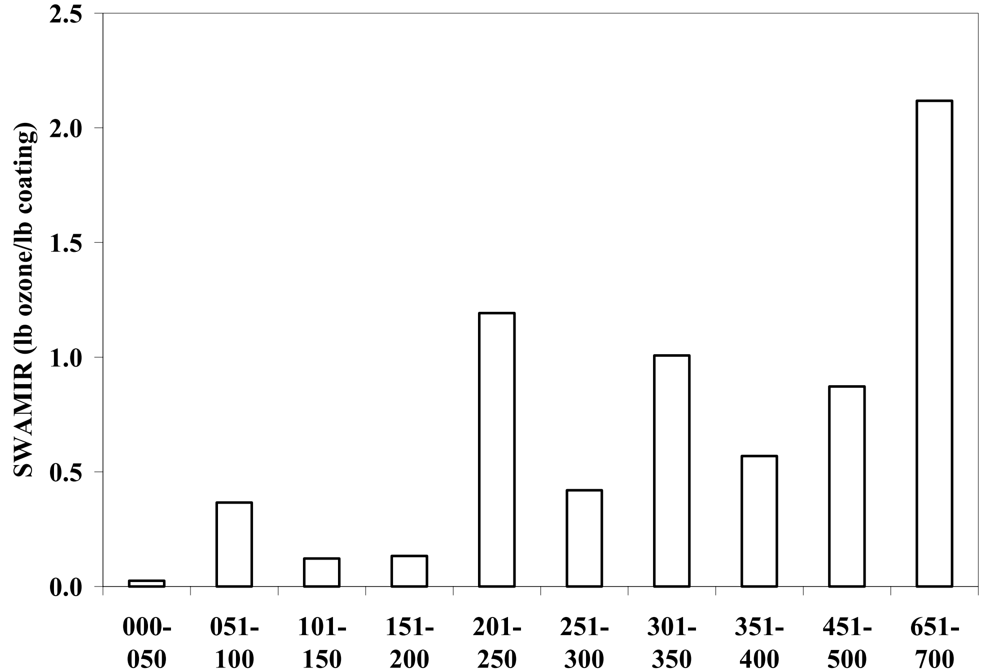
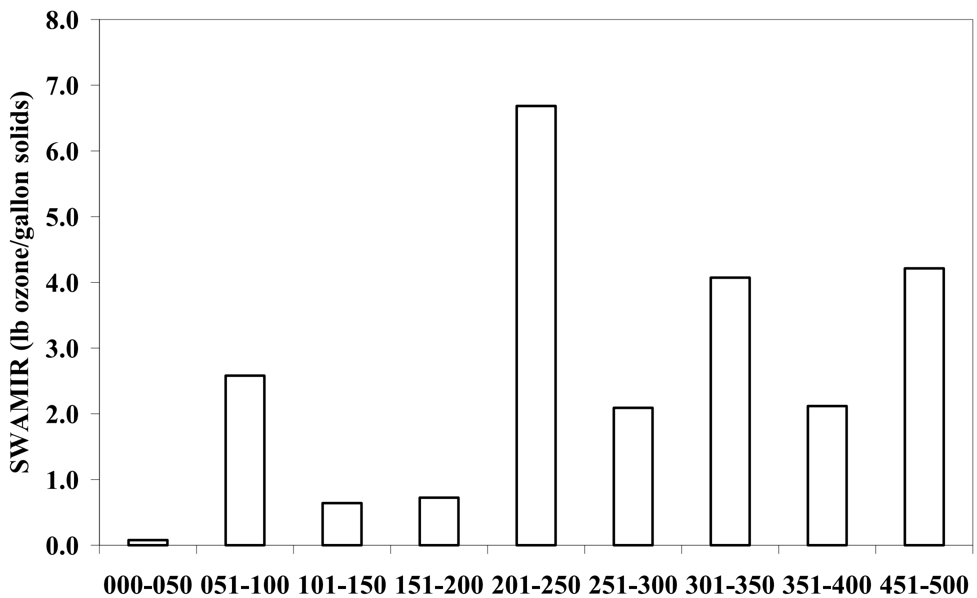


Figure 2-29
Floor (lb O3/gallon solids)



***Note: This chart does not include all products in this category. To improve chart resolution, upper VOC ranges with high SWAMIR values are not shown. Please refer to the Appendix to see the complete data for this category.**

Figure 2-30
Industrial Maintenance (lb O^3/lb coating)

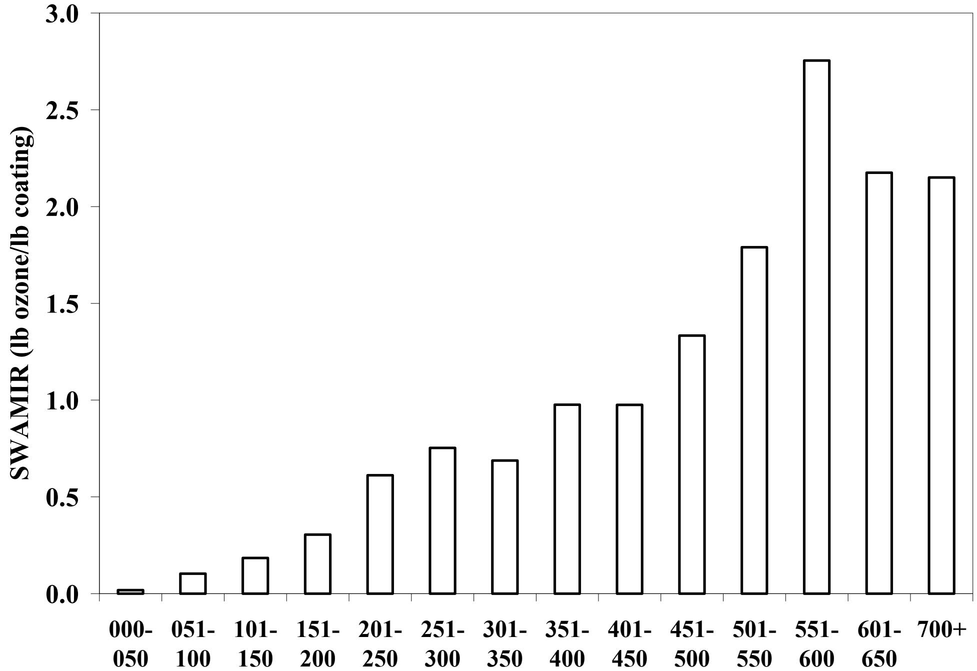
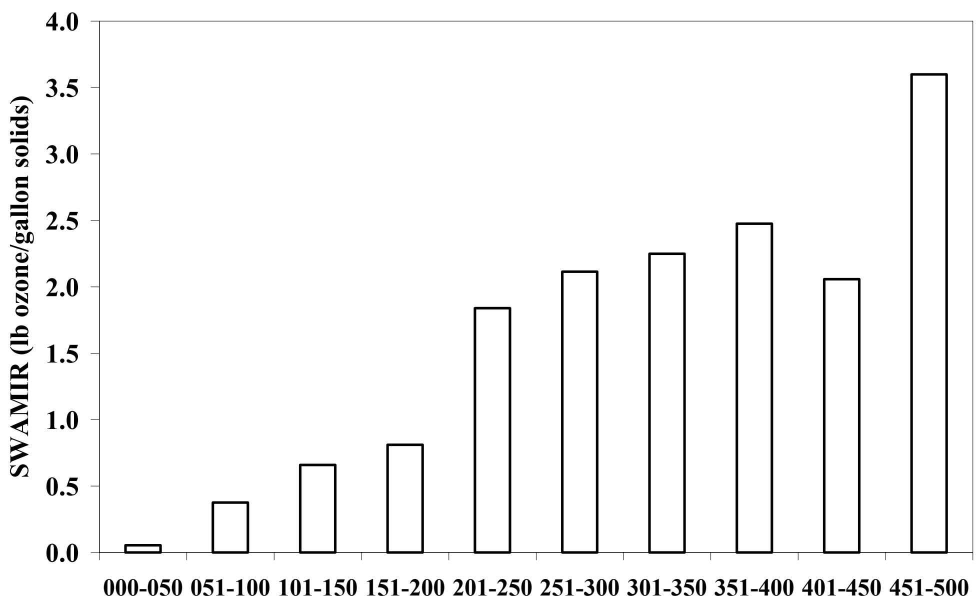


Figure 2-31
Industrial Maintenance (lb O^3/gallon solids)



***Note: This chart does not include all products in this category. To improve chart resolution, upper VOC ranges with high SWAMIR values are not shown. Please refer to the Appendix to see the complete data for this category.**

Figure 2-32
Lacquers (lb O^3/lb coating)

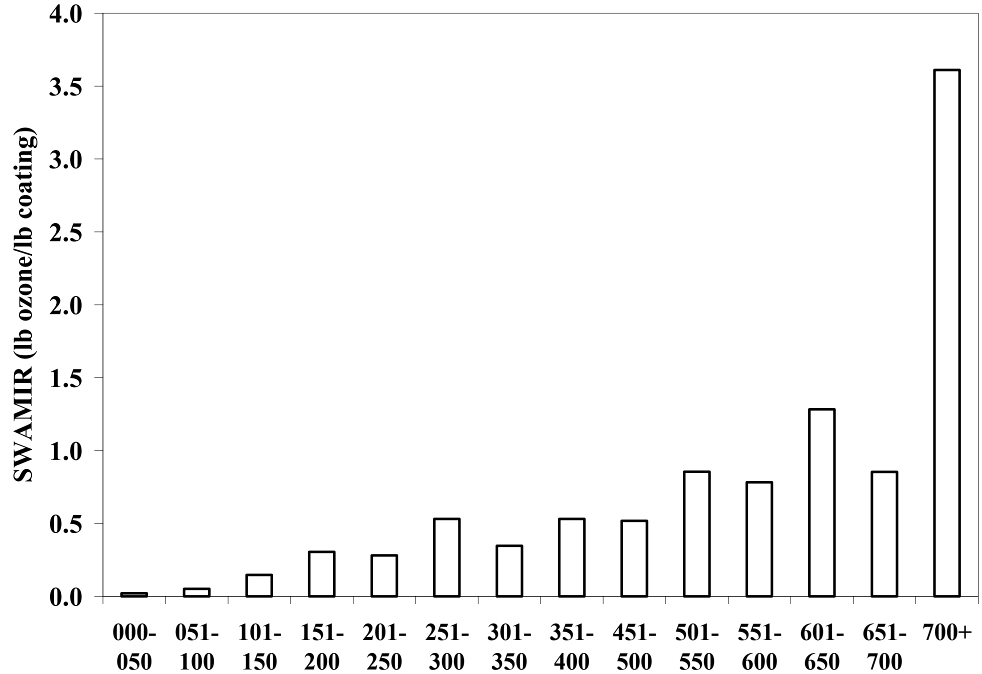
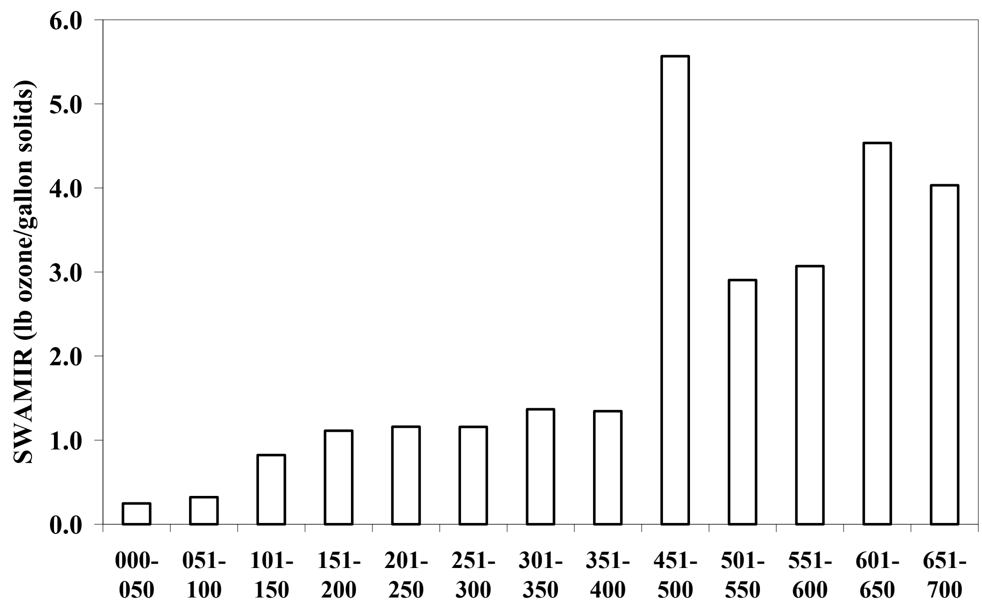


Figure 2-33
Lacquers (lb O^3/gallon solids)



***Note: This chart does not include all products in this category. To improve chart resolution, upper VOC ranges with high SWAMIR values are not shown. Please refer to the Appendix to see the complete data for this category.**

Figure 2-34
Metallic Pigmented (lb O3/lb coating)

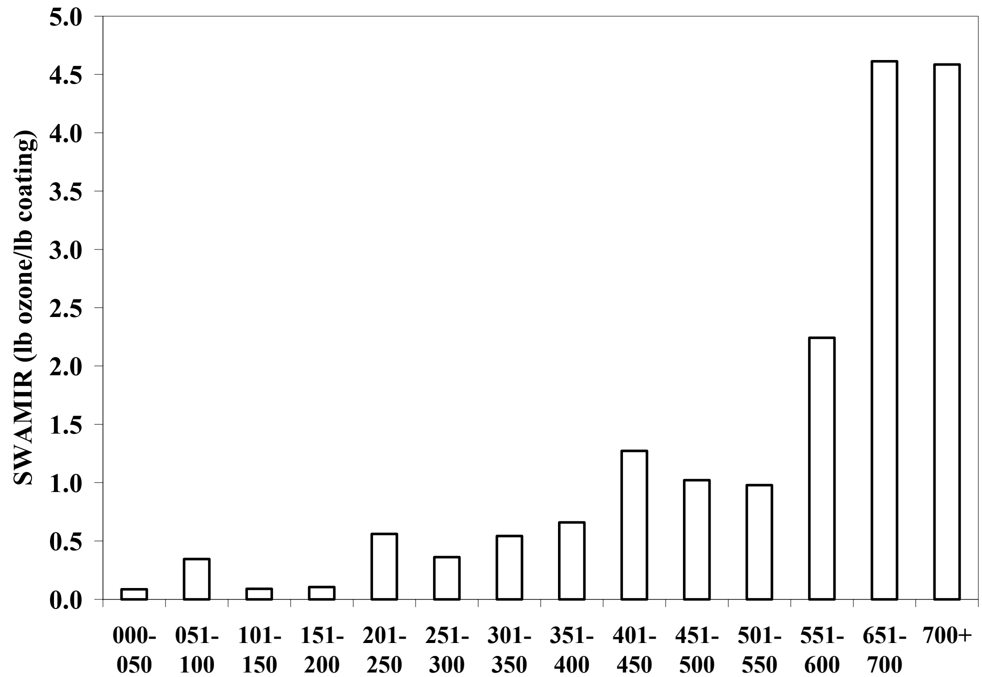
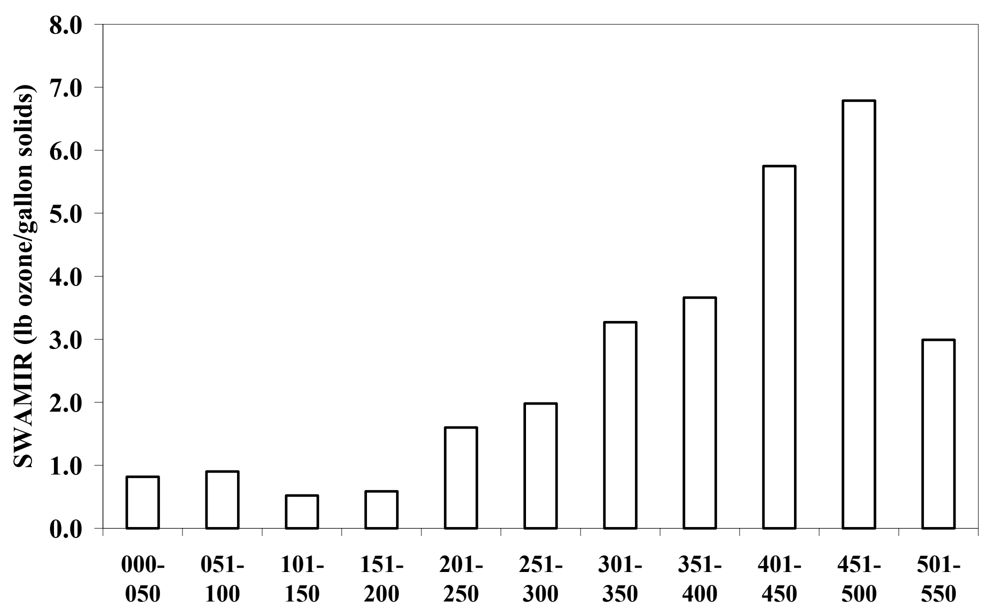


Figure 2-35
Metallic Pigmented (lb O3/gallon solids)



***Note: This chart does not include all products in this category. To improve chart resolution, upper VOC ranges with high SWAMIR values are not shown. Please refer to the Appendix to see the complete data for this category.**

Figure 2-36
Nonflat – High Gloss (lb O3/lb coating)

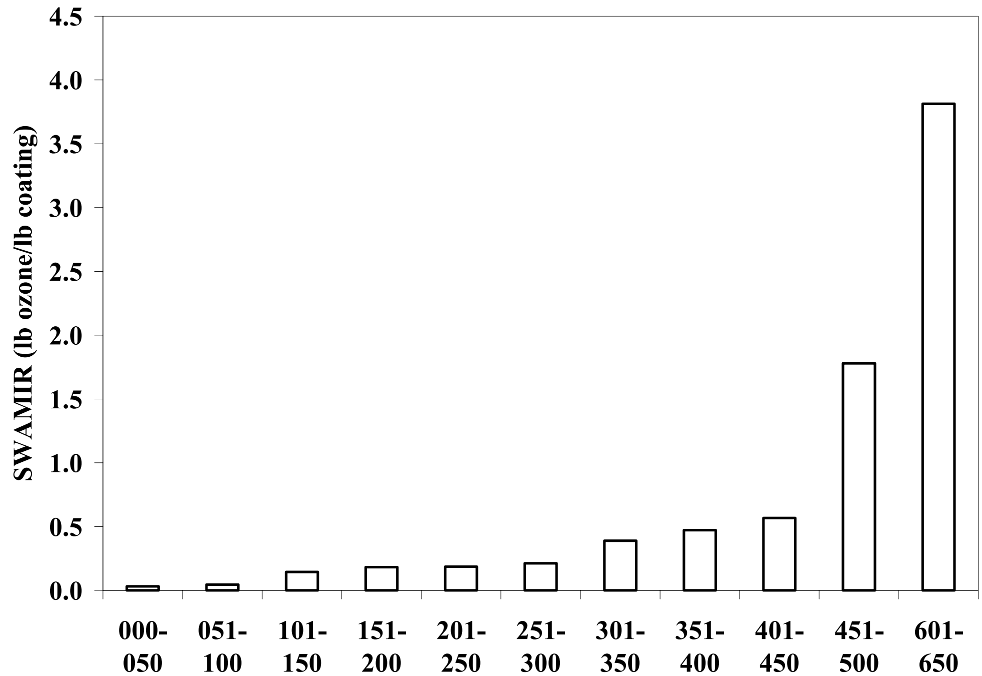
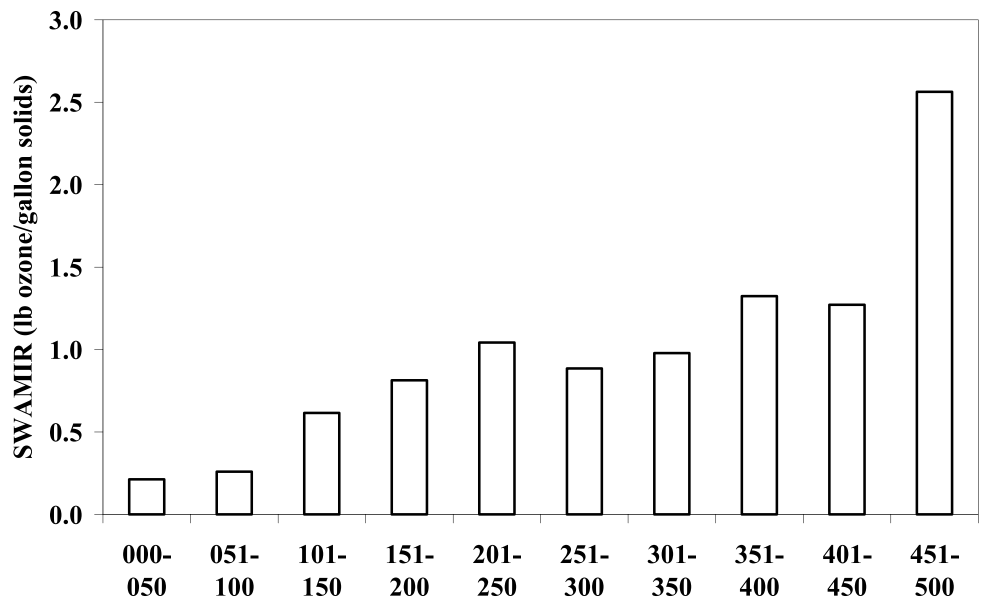


Figure 2-37
Nonflat – High Gloss (lb O3/gallon solids)



***Note: This chart does not include all products in this category. To improve chart resolution, upper VOC ranges with high SWAMIR values are not shown. Please refer to the Appendix to see the complete data for this category.**

Figure 2-38
Nonflat – Low Gloss (lb O3/lb coating)

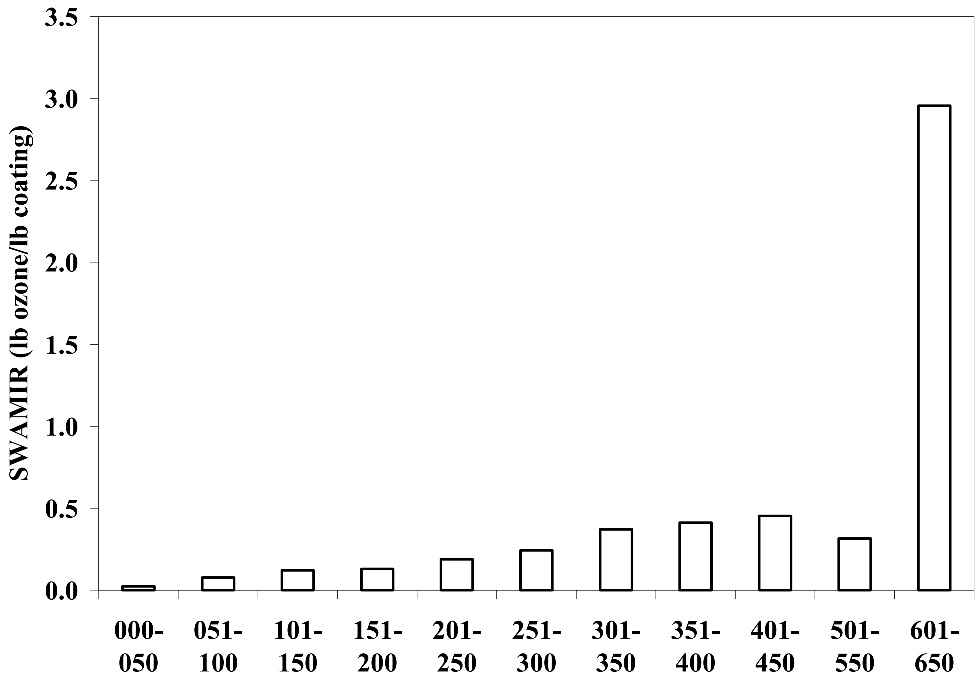
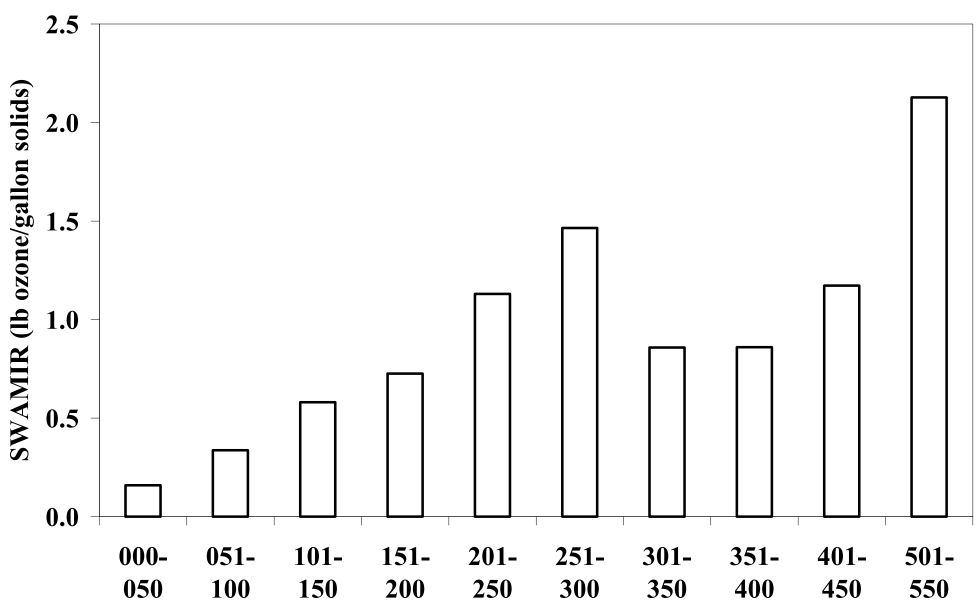


Figure 2-39
Nonflat – Low Gloss (lb O3/gallon solids)



***Note: This chart does not include all products in this category. To improve chart resolution, upper VOC ranges with high SWAMIR values are not shown. Please refer to the Appendix to see the complete data for this category.**

Figure 2-40
Nonflat – Medium Gloss (lb O^3/lb coating)

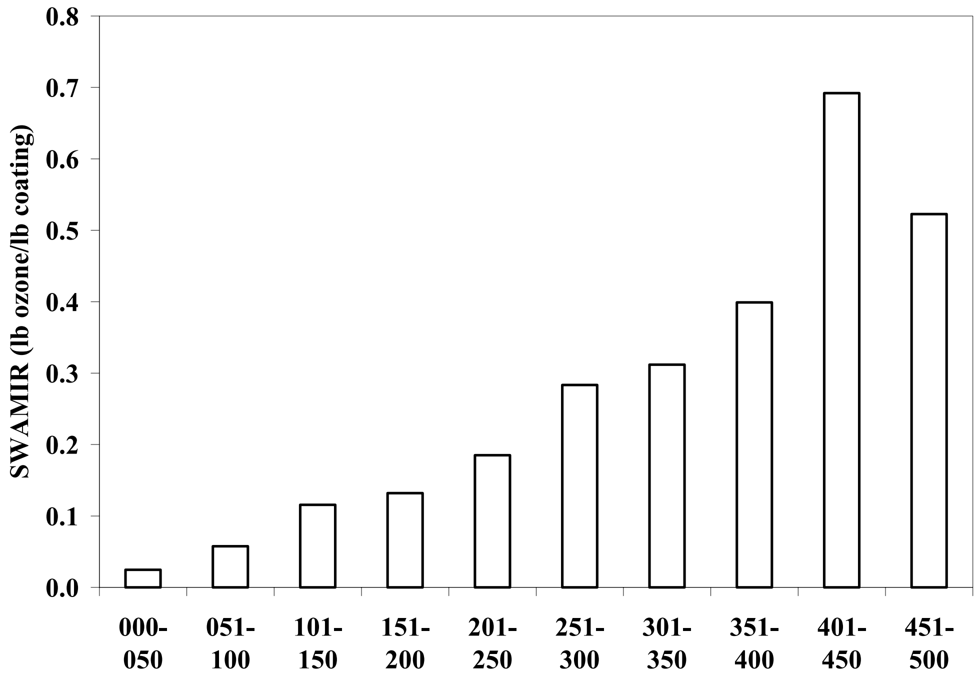


Figure 2-41
Nonflat – Medium Gloss (lb O^3/gallon solids)

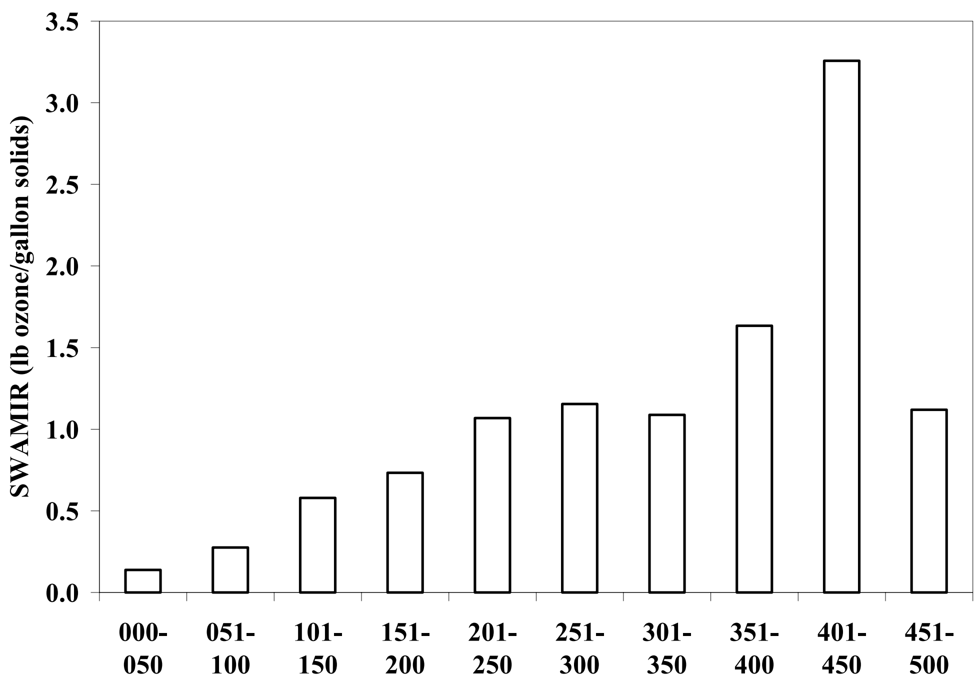


Figure 2-42
Primer, Sealer, Undercoater (lb O^3/lb coating)

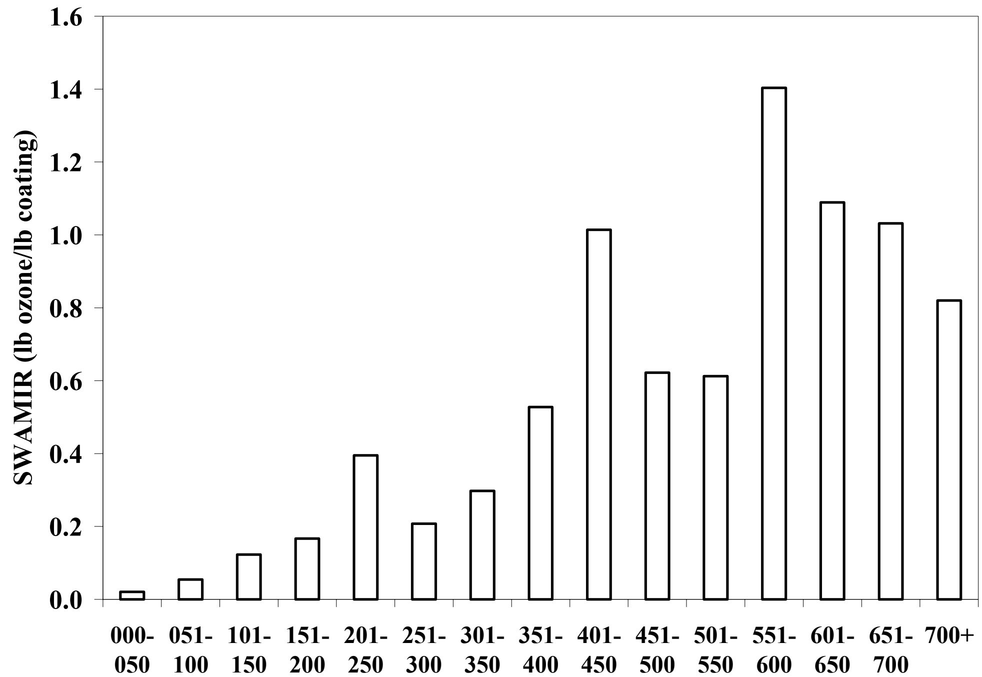
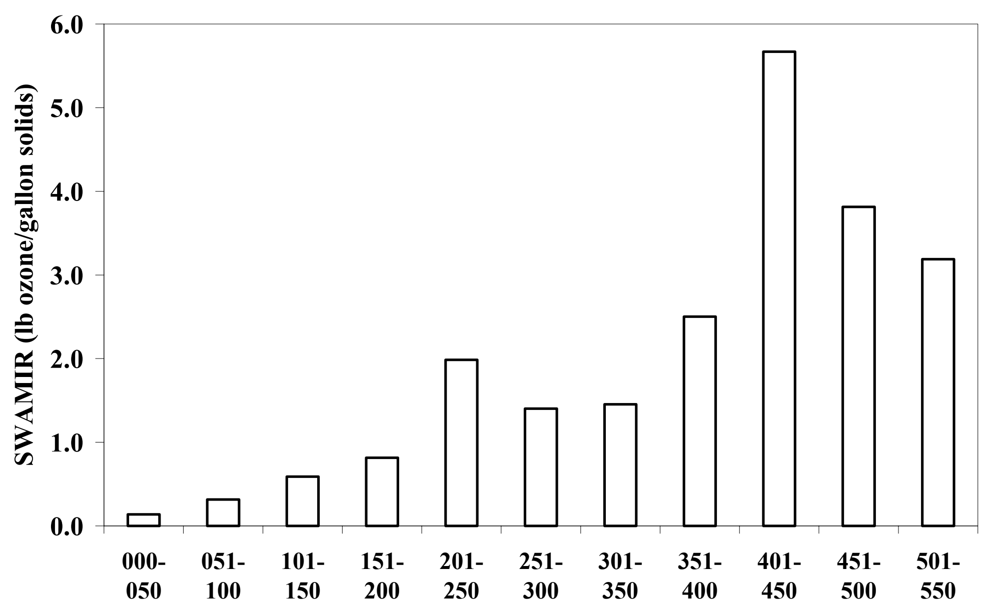


Figure 2-43
Primer, Sealer, Undercoater (lb O^3/gallon solids)



***Note: This chart does not include all products in this category. To improve chart resolution, upper VOC ranges with high SWAMIR values are not shown. Please refer to the Appendix to see the complete data for this category.**

Figure 2-44
Quick Dry Enamel (lb O3/lb coating)

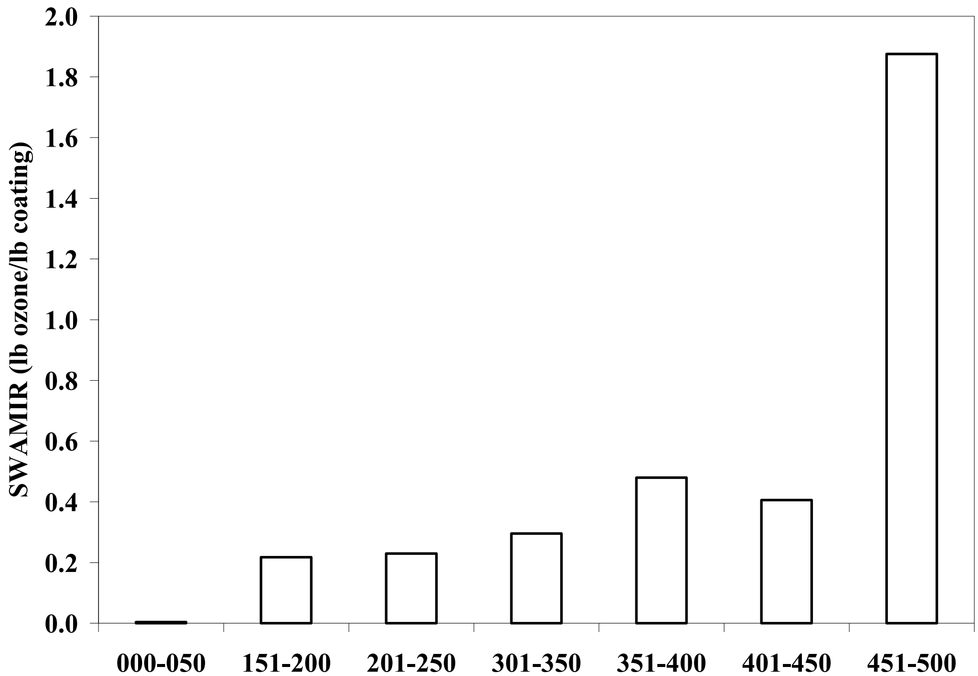


Figure 2-45
Quick Dry Enamel (lb O3/gallon solids)

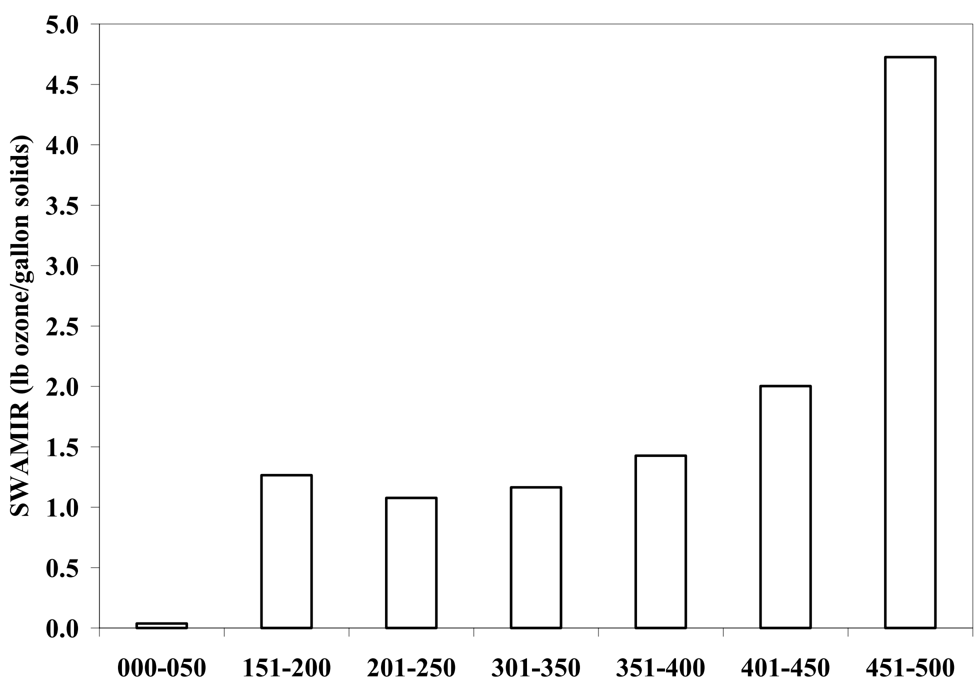


Figure 2-46
Quick Dry Primer, Sealer, Undercoater (lb O^3/lb coating)

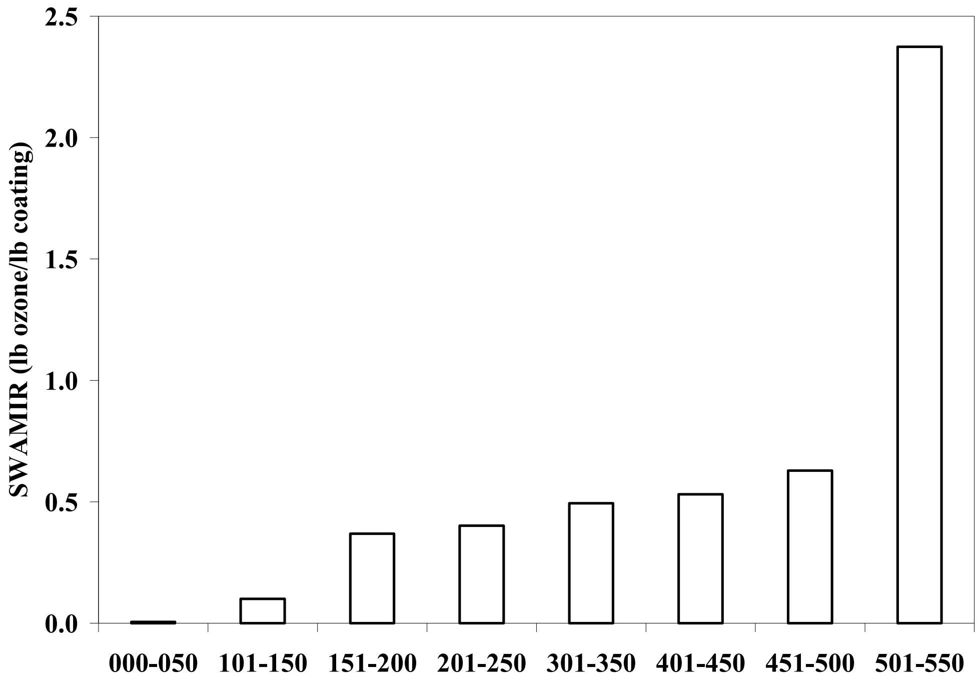
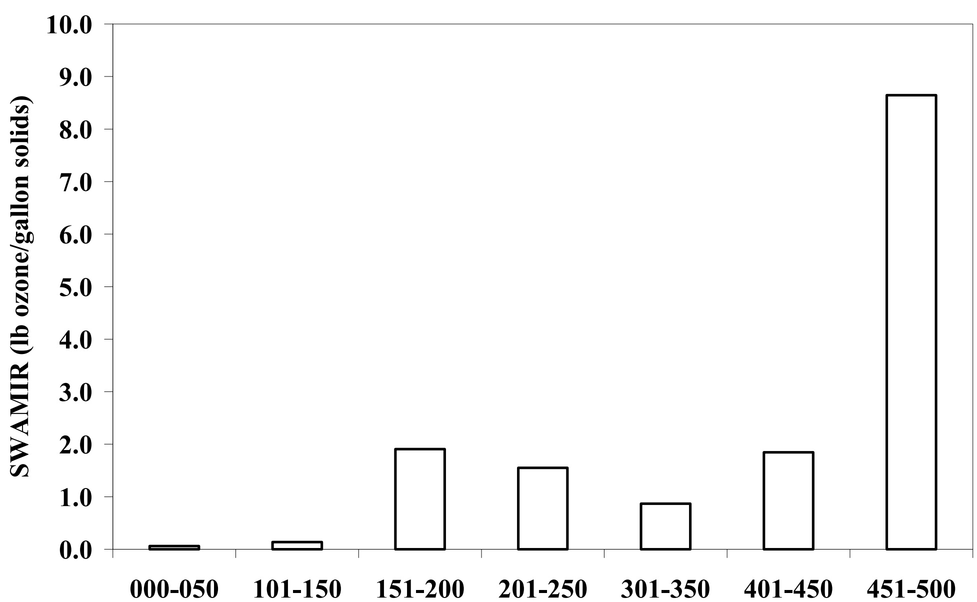


Figure 2-47
Quick Dry Primer, Sealer, Undercoater (lb O^3/gallon solids)



***Note: This chart does not include all products in this category. To improve chart resolution, upper VOC ranges with high SWAMIR values are not shown. Please refer to the Appendix to see the complete data for this category.**

Figure 2-48
Rust Preventative (lb O3/lb coating)

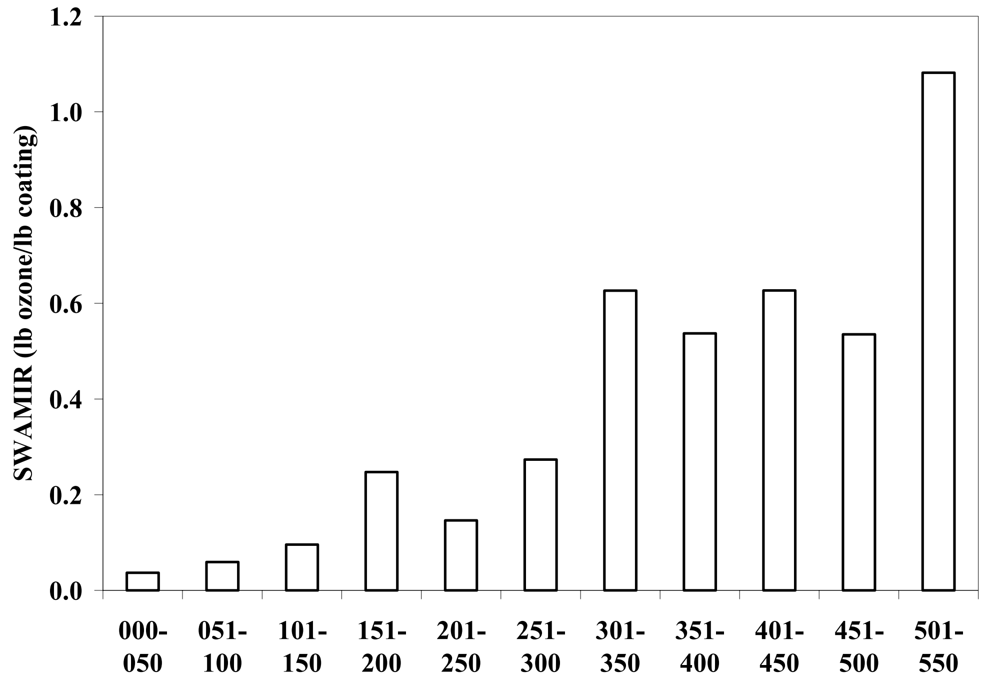


Figure 2-49
Rust Preventative (lb O3/gallon solids)

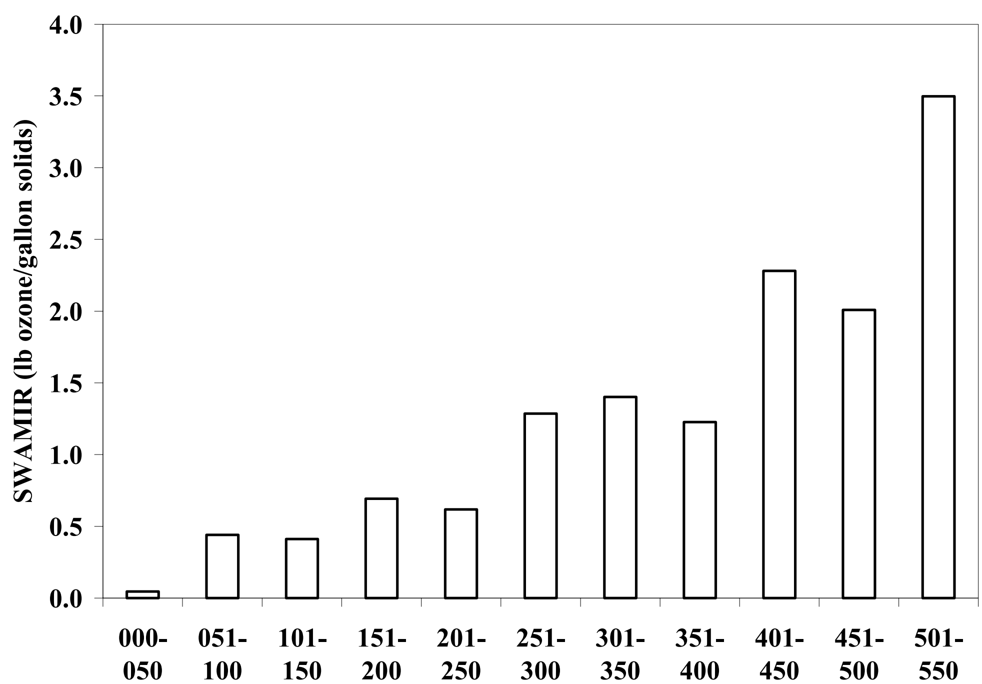


Figure 2-50
Specialty Primer, Sealer, Undercoater (lb O3/lb coating)

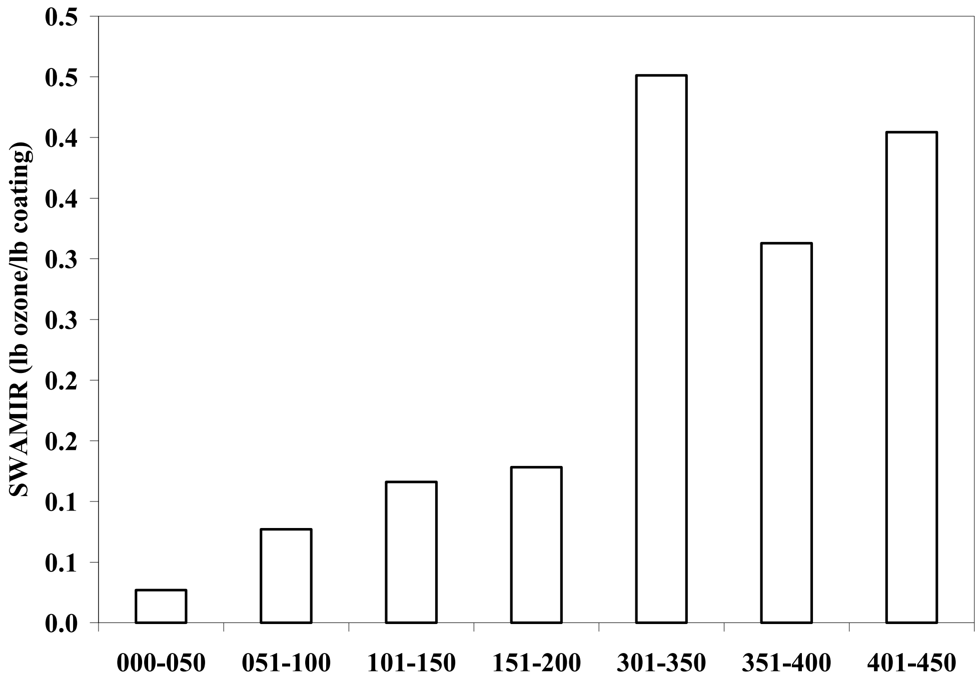


Figure 2-51
Specialty Primer, Sealer, Undercoater (lb O3/gallon solids)

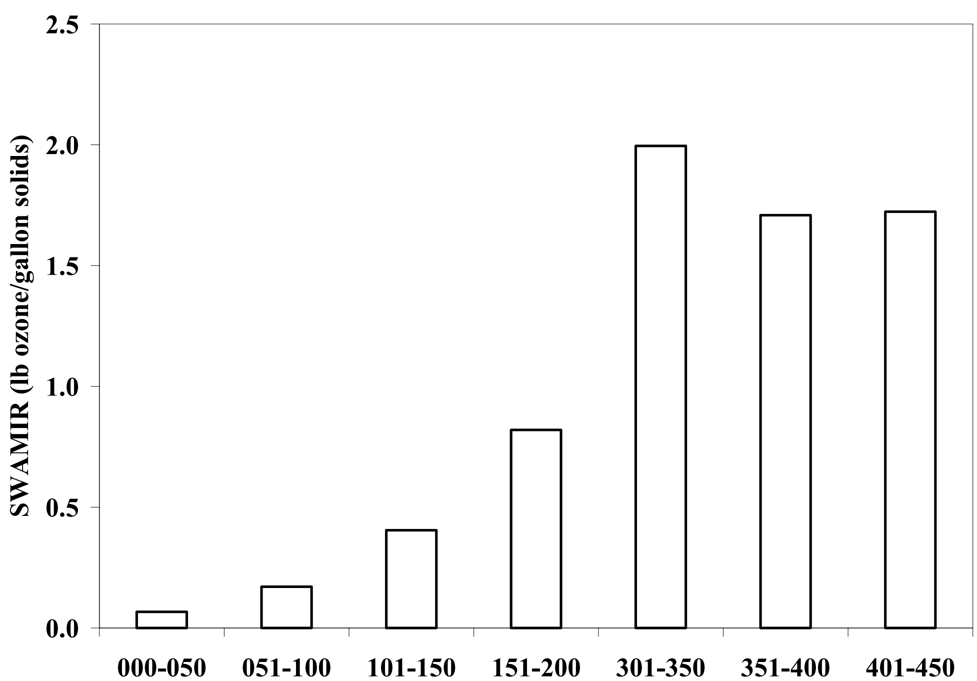


Figure 2-52
Stains – Clear/Semitransparent (lb O^3/lb coating)

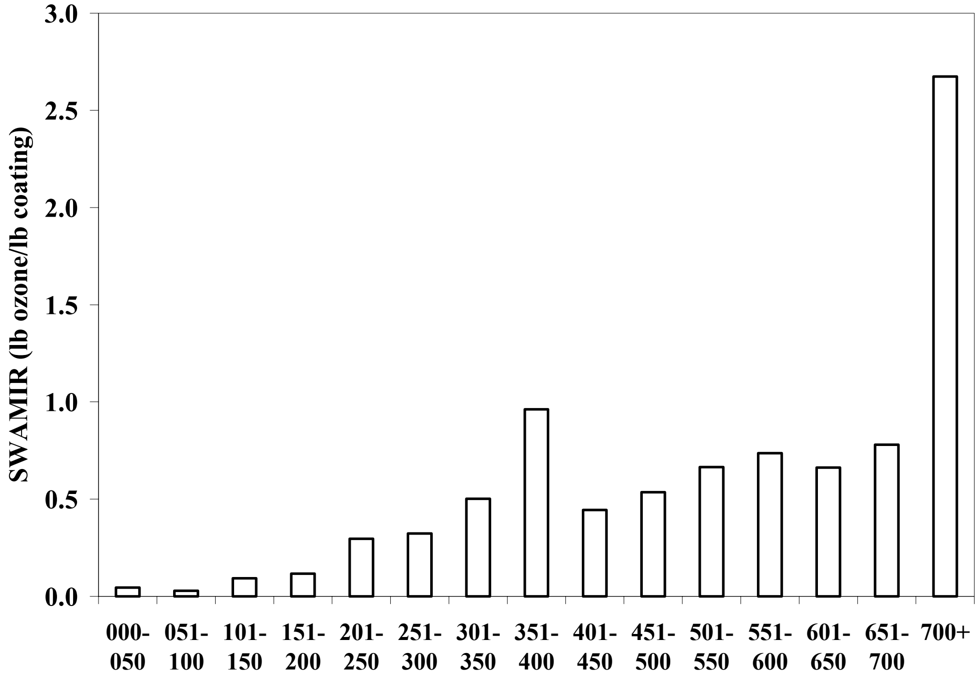
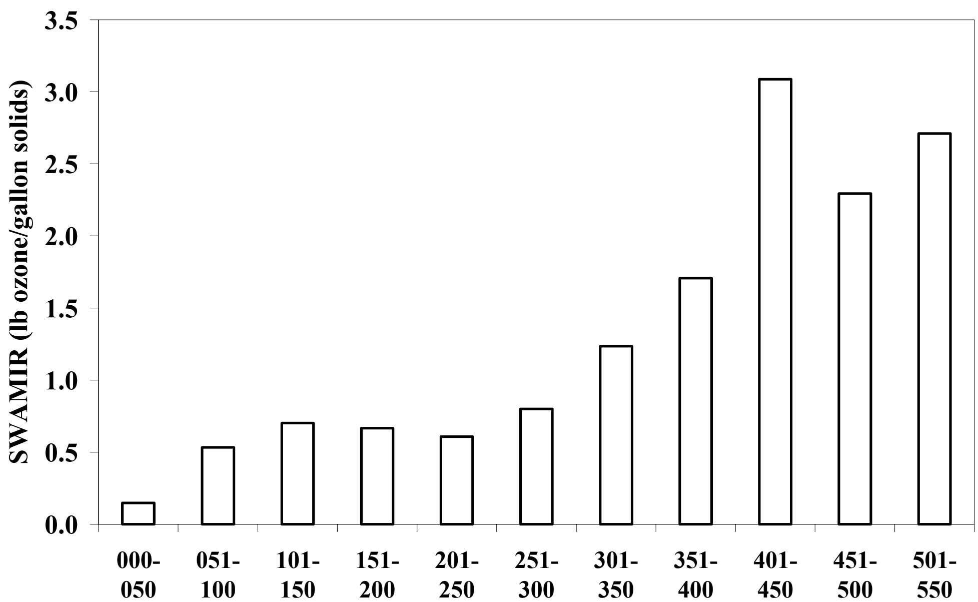


Figure 2-53
Stains – Clear/Semitransparent (lb O^3/gallon solids)



***Note: This chart does not include all products in this category. To improve chart resolution, upper VOC ranges with high SWAMIR values are not shown. Please refer to the Appendix to see the complete data for this category.**

Figure 2-54
Varnishes – Clear (lb O^3/lb coating)

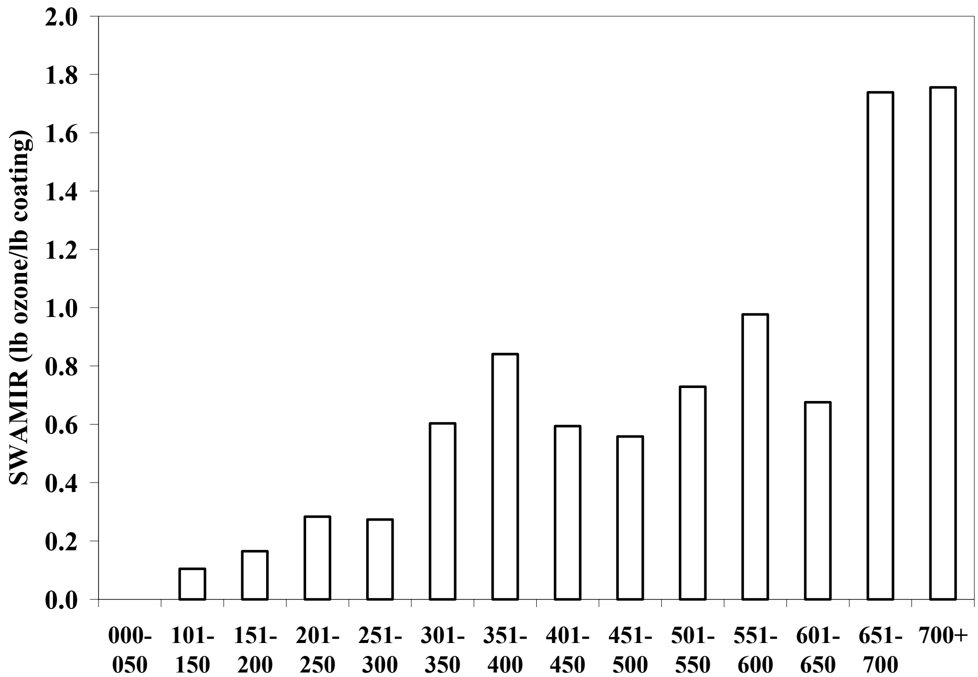
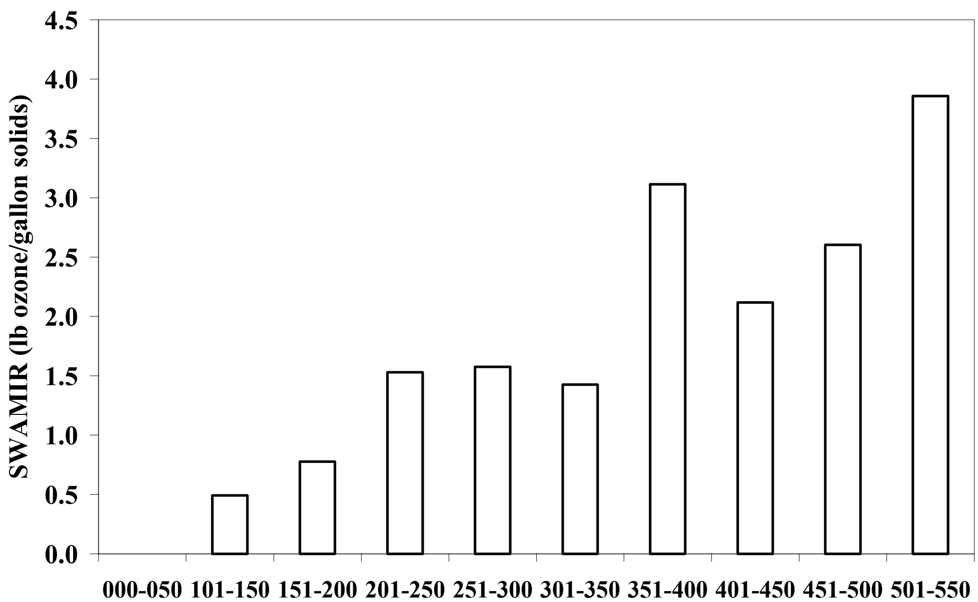


Figure 2-55
Varnishes – Clear (lb O^3/gallon solids)



***Note: This chart does not include all products in this category. To improve chart resolution, upper VOC ranges with high SWAMIR values are not shown. Please refer to the Appendix to see the complete data for this category.**

Figure 2-56
Waterproofing Concrete/Masonry Sealers (lb O^3/lb coating)

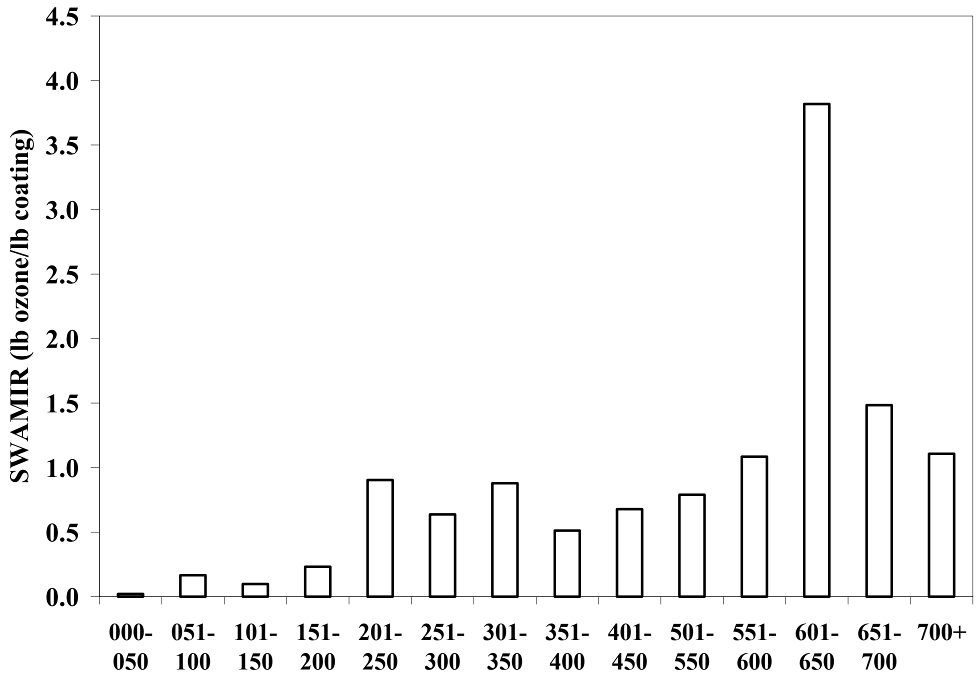
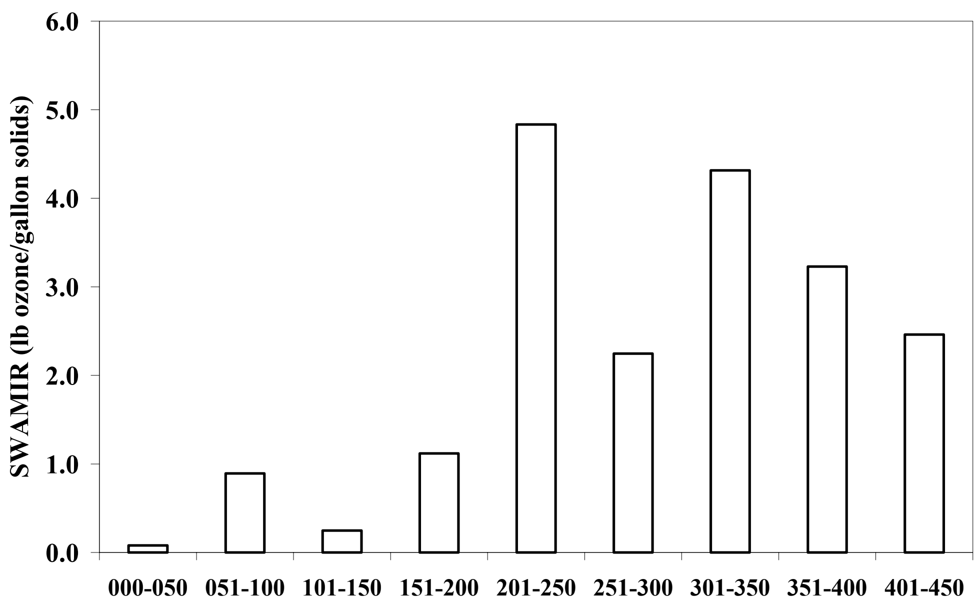


Figure 2-57
Waterproofing Concrete/Masonry Sealers (lb O^3/gallon solids)



***Note: This chart does not include all products in this category. To improve chart resolution, upper VOC ranges with high SWAMIR values are not shown. Please refer to the Appendix to see the complete data for this category.**

Figure 2-58
Waterproofing Sealers (lb O^3/lb coating)

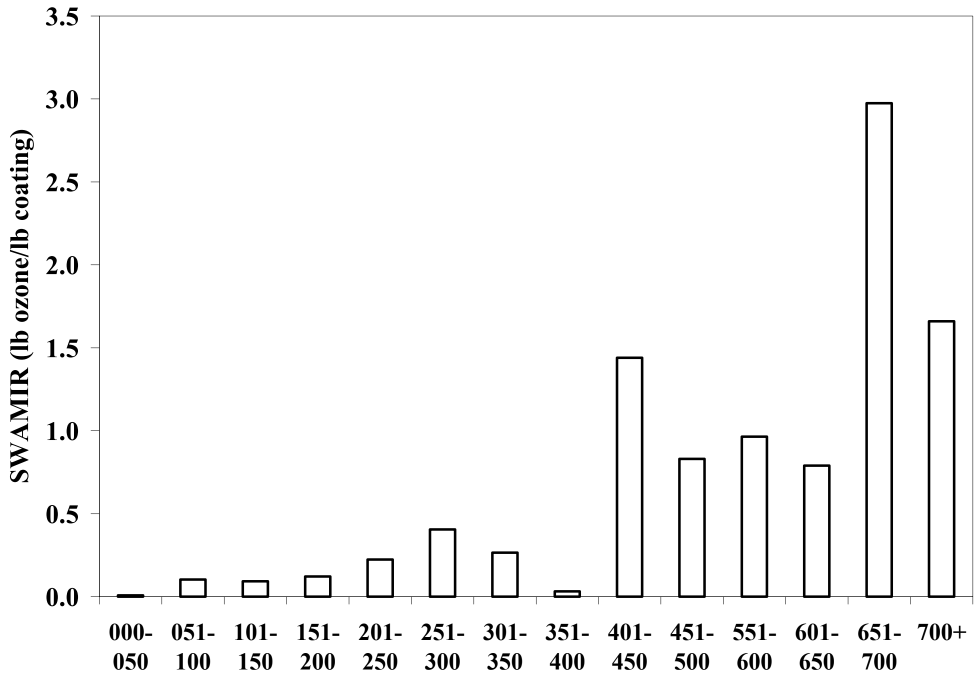
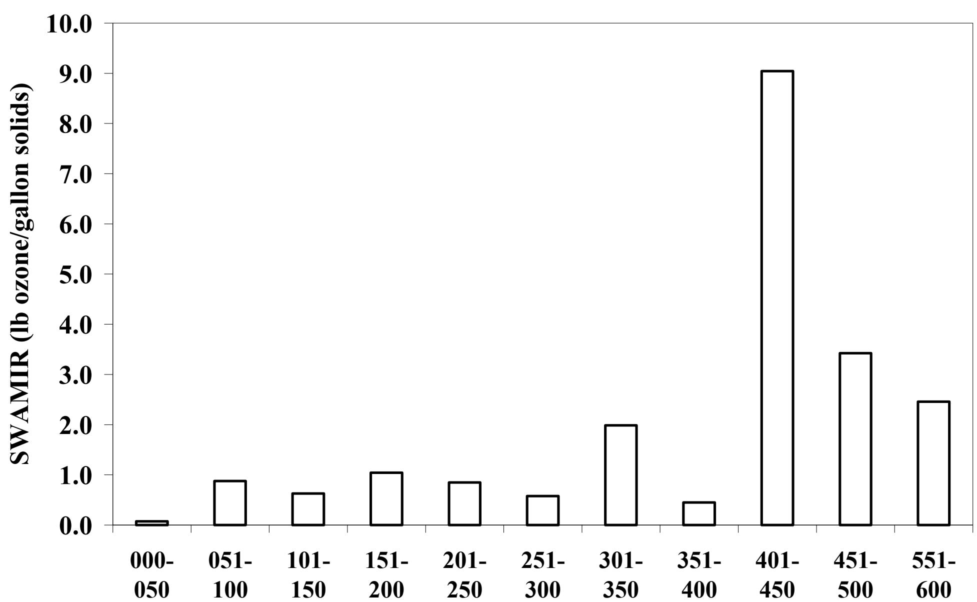


Figure 2-59
Waterproofing Sealers (lb O^3/gallon solids)



***Note: This chart does not include all products in this category. To improve chart resolution, upper VOC ranges with high SWAMIR values are not shown. Please refer to the Appendix to see the complete data for this category.**

Section 2.5 Ingredient Contributions To Reactivity

To identify opportunities for ozone reductions, it is important to know which ingredients contribute the most to a category's potential ozone creation. The following table focuses on the ingredients that are the primary contributors to either VOC emissions or maximum potential ozone totals for selected categories. Table 2-4 only lists ingredients that represent more than 10% of the total maximum potential ozone for a category or ingredients that represent more than 10% by weight of the total volatile ingredients (excluding water). It highlights categories where it may be possible to replace a more reactive ingredient with one that is less reactive.

Table 2-4: ***Ingredients That Contribute the Most to Emissions and Potential Ozone***

Category	CAS	Ingredient	MIR (g O^3/ g ingr)	Ingred. Qty. (tpd)	Max. Ozone (tpd)	% of Total Volatiles For Category	% of Total Max. Ozone From Category
Bituminous Roof		Bin 15 Hydrocarbon Solvent	1.82	0.53	0.96	81%	62%
		Bin 22 Hydrocarbon Solvent	7.51	0.06	0.44	9%	29%
Flat	107211	Ethylene Glycol	3.63	3.48	12.65	25%	34%
	124685	2-Amino-2-Methyl-1-Propanol	15.08	0.61	9.19	4%	25%
	25265774	2,2,4-Trimethyl-1,3-Pentanediol Isobutyrate	0.89	6.46	5.75	47%	16%
	57556	Propylene Glycol	2.75	1.84	5.05	13%	14%
Floor	9986	Unknown	2.73	1.36	3.72	60%	56%
		Bin 22 Hydrocarbon Solvent	7.51	0.12	0.88	5%	13%
	29911271	Dipropylene Glycol Monopropyl Ether	2.13	0.24	0.51	11%	8%
Industrial Maintenance	1330207	Xylene	7.48	0.67	5.01	15%	34%
		Bin 11 Hydrocarbon Solvent	0.91	0.59	0.54	14%	4%
Lacquers	67641	Acetone	0.43	4.02	1.73	55%	19%
	1330207	Xylene	7.48	0.18	1.34	2%	15%
	111762	2-Butoxy Ethanol	2.90	0.33	0.94	4%	10%
	123864	Butyl Acetate, 1-	0.89	0.87	0.78	12%	8%
Metallic Pigmented		Bin 15 Hydrocarbon Solvent	1.82	1.35	2.45	62%	41%
		Bin 22 Hydrocarbon Solvent	7.51	0.32	2.43	15%	40%
Nonflat - High Gloss	107211	Ethylene Glycol	3.63	0.35	1.26	26%	33%
	124685	2-Amino-2-Methyl-1-Propanol	15.08	0.05	0.79	4%	21%
	57556	Propylene Glycol	2.75	0.17	0.48	13%	13%
	5444757	2-Ethylhexyl Benzoate	2.73	0.17	0.46	13%	12%
	25265774	2,2,4-Trimethyl-1,3-Pentanediol Isobutyrate	0.89	0.33	0.30	25%	8%

Table 2-4: *Ingredients That Contribute the Most to Emissions and Potential Ozone*

Category	CAS	Ingredient	MIR (g O^3/ g ingr)	Ingred. Qty. (tpd)	Max. Ozone (tpd)	% of Total Volatiles For Category	% of Total Max. Ozone From Category
Nonflat - Low Gloss	107211	Ethylene Glycol	3.63	2.61	9.47	39%	51%
	57556	Propylene Glycol	2.75	0.93	2.56	14%	14%
	124685	2-Amino-2-Methyl-1-Propanol	15.08	0.15	2.26	2%	12%
	25265774	2,2,4-Trimethyl-1,3-Pentanediol Isobutyrate	0.89	1.94	1.72	29%	9%
Nonflat - Medium Gloss	107211	Ethylene Glycol	3.63	3.31	12.02	28%	41%
	57556	Propylene Glycol	2.75	2.70	7.41	23%	25%
	25265774	2,2,4-Trimethyl-1,3-Pentanediol Isobutyrate	0.89	3.83	3.41	33%	12%
Primer, Sealer, and Undercoater	107211	Ethylene Glycol	3.63	2.59	9.41	40%	51%
	124685	2-Amino-2-Methyl-1-Propanol	15.08	0.24	3.68	4%	20%
	25265774	2,2,4-Trimethyl-1,3-Pentanediol Isobutyrate	0.89	1.67	1.48	26%	8%
		Bin 11 Hydrocarbon Solvent	0.91	0.76	0.69	12%	4%
Quick Dry Enamel		Bin 11 Hydrocarbon Solvent	0.91	2.33	2.12	72%	46%
		Bin 10 Hydrocarbon Solvent	2.03	0.34	0.70	11%	15%
Quick Dry Primer, Sealer, and Undercoater		Bin 6 Hydrocarbon Solvent	1.41	0.63	0.89	62%	53%
		Bin 11 Hydrocarbon Solvent	0.91	0.22	0.20	22%	12%
Rust Preventative		Bin 10 Hydrocarbon Solvent	2.03	1.87	3.79	21%	24%
		Bin 11 Hydrocarbon Solvent	0.91	3.86	3.51	44%	23%
		Bin 15 Hydrocarbon Solvent	1.82	1.21	2.20	14%	14%
	1330207	Xylene	7.48	0.25	1.88	3%	12%
Specialty Primer, Sealer, and Undercoater		Bin 22 Hydrocarbon Solvent	7.51	0.62	4.66	10%	40%
		Bin 11 Hydrocarbon Solvent	0.91	4.45	4.05	74%	35%
Stains - Clear/ Semitransparent		Bin 11 Hydrocarbon Solvent	0.91	3.87	3.52	59%	40%
Varnishes - Clear		Bin 11 Hydrocarbon Solvent	0.91	2.77	2.52	70%	46%
		Bin 15 Hydrocarbon Solvent	1.82	0.41	0.75	10%	14%

Table 2-4: ***Ingredients That Contribute the Most to Emissions and Potential Ozone***

Category	CAS	Ingredient	MIR (g O^3/ g ingr)	Ingred. Qty. (tpd)	Max. Ozone (tpd)	% of Total Volatiles For Category	% of Total Max. Ozone From Category
Waterproofing Concrete/Masonry Sealers		Bin 22 Hydrocarbon Solvent	7.51	0.42	3.12	11%	37%
		Bin 6 Hydrocarbon Solvent	1.41	0.65	0.92	17%	11%
	67641	Acetone	0.43	0.55	0.24	14%	3%
	98566	4-Chlorobenzotrifluoride	0.11	0.58	0.06	15%	1%
Waterproofing Sealers		Bin 11 Hydrocarbon Solvent	0.91	0.61	0.55	39%	16%
	34590948	Dipropylene Glycol Methyl Ether	2.46	0.18	0.45	12%	13%
	107211	Ethylene Glycol	3.63	0.12	0.43	7%	13%

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Chapter 3 – Reactivity-Related Research Projects

This section describes some of the research projects that have been funded by ARB to help expand our understanding of architectural coatings and improve regulatory efforts. These research projects were coordinated with the ARB's Reactivity Research Advisory Committee (RRAC), which includes representatives from coating manufacturers, solvent manufacturers, and regulatory agencies.

Section 3.1 ARB-Funded Research

ARB funded a $300,000 architectural coating reactivity project with UC Riverside that began in 2001. The final report for this project was completed in March 2005 (http://www.arb.ca.gov/research/apr/past/00-333.pdf). Researchers used a state-of-the-art environmental chamber to verify the chemical mechanisms that determine the reactivity of Texanol® and several hydrocarbon solvents that are commonly used in architectural coatings. Table 3-1 describes the hydrocarbon solvents that were tested during the project.

Table 3-1: ***Hydrocarbon Solvents Tested in Environmental Chamber***

Solvent	ASTM Designation	Aromatic Content	ASTM Distillation Range (ºF)	ARB Bin #	Description
VM&P Naphtha	D3735, Type IV	0.1%	235-310	6	Primarily C7-C9 Mixed Alkanes. Petroleum Distillate Derived.
Dearomatized Mineral Spirits	D235, Type IC	0%	300-415	11	Primarily C10-C12 Mixed Alkanes. Petroleum Distillate Derived.
Reduced Aromatics Mineral Spirits	D235, Type IB	6%	300-415	14	Primarily C10-C12 Mixed Alkanes. Petroleum Distillate Derived.
Regular Mineral Spirits	D235, Type IA	19%	300-415	15	Primarily C10-C12 Mixed Alkanes. Petroleum Distillate Derived.
Aromatic 100	D3734, Type I	100%	300-355	22	Primarily C9-C10 Alkylbenzenes. Petroleum Distillate Derived.
Synthetic Isoparaffinic Alkanes	D235, Type III C-1	0%	300-415	12	Primarily C10-C12 Branched Alkanes. Synthetic Mixture.

Table 3-2 contains the baseline MIR values and the MIR values that resulted from the research project. For hydrocarbon solvents, baseline MIR values were obtained from ARB's Aerosol Coatings Regulation and the hydrocarbon solvent bin system (California Code of Regulations, Title 17, Section 94701.) For most of the solvents tested, the results of the research confirmed the baseline MIR values. However, the research indicated that the baseline MIR may be too low for the Synthetic Isoparaffinic Alkanes (i.e., Odorless

Mineral Spirits) in Bin 12. Additional research may be needed to improve the computer modeling for synthetic hydrocarbons. At this time, ARB has not proposed a change to the MIR table to adjust for Bin 12 synthetic hydrocarbons.

Table 3-2: ***Results of ARB-Funded Reactivity Research Project***

Solvent	Baseline MIR	MIR Based on Research Project
Isobutyrate Monoesters of 2,2,4-Trimethyl-1,3-Pentanediol (Texanol®)	0.88	0.88
VM&P Naphtha (D3735, Type IV)	1.41	1.35
Dearomatized Mineral Spirits (D235, Type IC)	0.91	0.96
Reduced Aromatics Mineral Spirits (D235, Type IB)	1.21	1.26
Regular Mineral Spirits (D235, Type IA)	1.82	1.97
Aromatic 100 (D3734, Type I)	7.51	7.70
Synthetic Isoparaffinic Alkanes (D235, Type III C-1)	0.81	1.1-1.5

Section 3.2 SCAQMD-Funded Research

In 2003, SCAQMD provided $200,000 to UC Riverside to conduct additional reactivity research. Four compounds were tested in the environmental chamber, including two that are major ingredients in water-based coatings (ethylene glycol and propylene glycol.) The final report for this project was completed in July 2005 (http://pah.cert.ucr.edu/~carter/coatings/SCAQcham.pdf).
Table 3-1 describes the hydrocarbon solvents that were tested during the project.

Table 3-3: ***Results of SCAQMD-Funded Reactivity Research Project***

Solvent	Baseline MIR	MIR Based on Research Project
Ethylene Glycol	3.36	3.63
Propylene Glycol	2.74	2.74
2-(2-Butoxyethoxy)-Ethanol (Diethylene Glycol Monobutyl Ether)	2.86	2.86
Benzyl Alcohol	none	4.89